AMBIENT CONCENTRATIONS OF PEROXYACETYL NITRATE (PAN), PEROXYPROPIONYL NITRATE (PPN) AND PERCHLOROETHYLENE (PCE) IN AZUSA, CA, FEBRUARY 2001 – SEPTEMBER 2003

Draft final report, December 2005

Contract 99-703, Task 3

Prepared for: **Research Division**

California Air Resources Board,

1001 I Street,

Sacramento, CA 95814

Prepared by: **Eric Grosjean and Daniel Grosjean**

DGA, Inc., 4526 Telephone Road, Suite 205

Ventura, CA 93003

Long Term Measurements of Peroxy Acetyl Nitrate (PAN) in Southern California

Dr. Ash Lashgari
Research Division of Air Resources Board
California Environmental Protection Agency

Introduction

On December 17, 1999 and due to documented impacts of leakage into ground water and consequent hazards, Methyl Tertiary Butyl Ether (MTBE), a fuel additive, was banned in California. Although some new fuel formulations may not require MTBE or other additives to provide carbon monoxide benefits, in many fuel formulations MTBE has been replaced with Ethanol. Atmospheric reactions of Ethanol with vehicle exhaust gases produce acetaldehyde leading to PAN formation that is an eye irritant and a reservoir of nitrogen dioxide. Nevertheless, the passage in June 2003 of the "Ethanol Mandate" in the federal energy bill has required use of Ethanol as a fuel additive. To study the potential effects of the "Ethanol Mandate," Air Resources Board (ARB) conducted a detailed analysis of available data on PAN and its transport, chemical transformation, and eventual fate (Grosjean, 1999). After that report, ARB also began a long term monitoring program of PAN, PPN, and PCE in southern California. Analyses of all available data for the monitoring program that began in January 2000 and ended on September 24, 2003 is the subject of this summary.

Methods

Among many available methods, PAN has been measured using Long-Path Fourier Transform Infrared Spectroscopy (Tuazon, et al., 1981), gas chromatography with electron capture detection (GC-ECD) (Grosjean, D., 1983), and the luminescence approach (Fitz, D. 2004). ARB Monitoring and Laboratory Division staff deployed two automated GC-ECD units purchased from Met Con, Inc. (2005) at Burbank and Azusa South Coast Air Quality Management routine air quality stations. At Burbank, measurements were taken from January to September 2000 and at Azusa, measurements continued from January 2000 to March 2002. DGA, Inc. staff with substantial expertise and many years of experience in PAN measurements operated their own GC-ECD unit at Azusa from February 22, 2001 to September 24, 2003. The two PAN data sets overlap for a substantial period of time allowing comparison of the two measurement methods. In addition to PAN, DGA, Inc. measurements include PPN and PCE data.

Method Comparison

Both data sets were reported on a sub-hourly basis (DGA 4 measurements per hour and Met Con 6 measurements per hour). To allow for a comparison, both data sets were converted to hourly measurements. Figure 1 describes how well the methods compared:

Met Con DGA Comparison

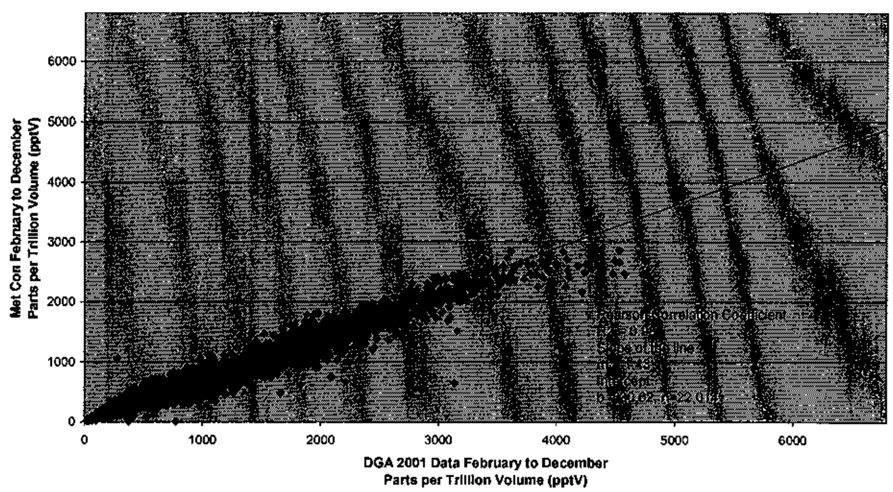

Figure 1: Comparison of Available DGA and Met Con PAN data.

With correlation coefficient of nearly 1 (0.98), DGA and PAN methods agree well. However, slope of 1.43 suggests that Met Con instrument may underestimate DGA data by more than 1/3. Intercept of 30 pptV is not as significant as the slope. To investigate potential trends and other issues at Azusa, DGA data had to be adjusted using this slope and intercept. Comparison of DGA and Unisearch luminescence PAN data during the Los Angeles Free Radical Study (Mackay, 1994) suggest that DGA and Met Con PAN data are indeed well correlated.

DGA Unisearch Comparison

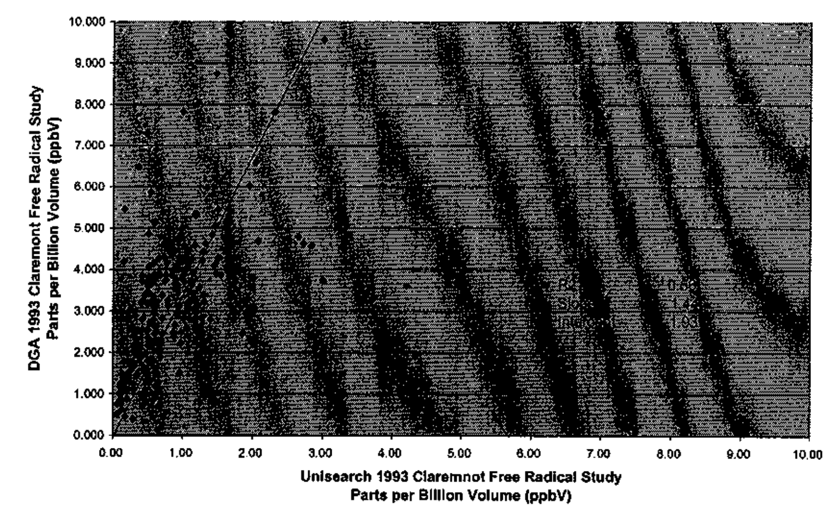

Figure 2: Comparison of Available DGA and Unisearch PAN data, September 1993.

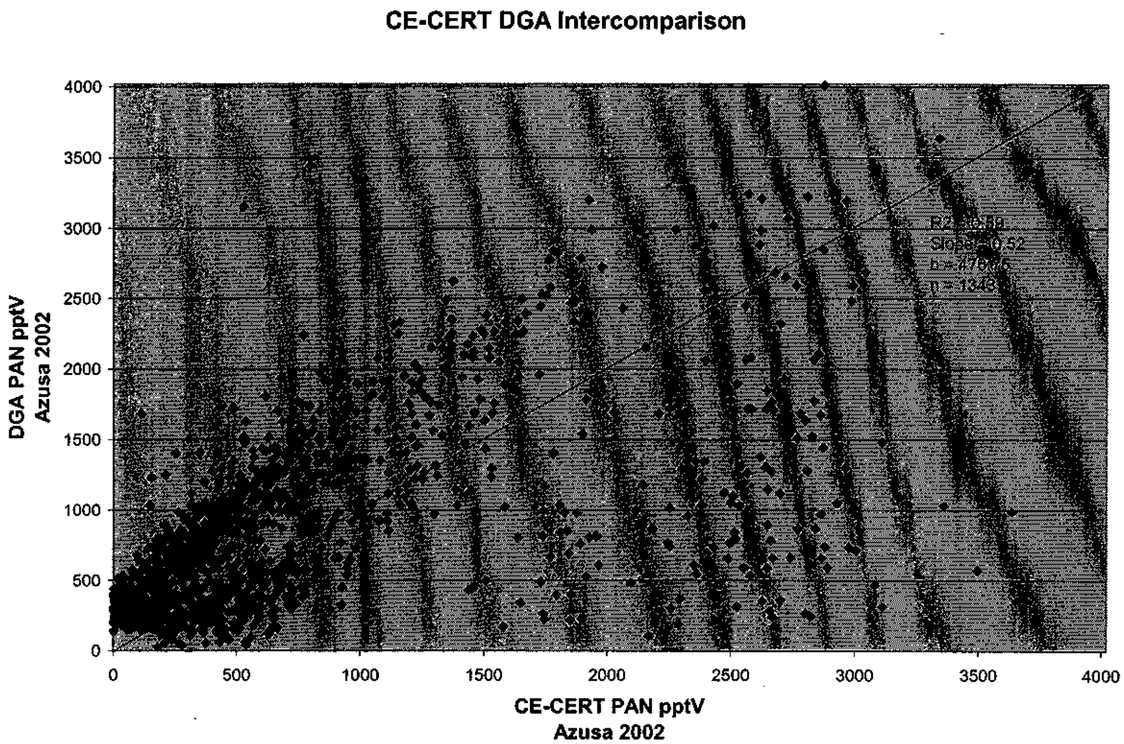

Figure 3: Comparison of Available DGA and CE-CERT PAN data, July 31 to December 2, 2002

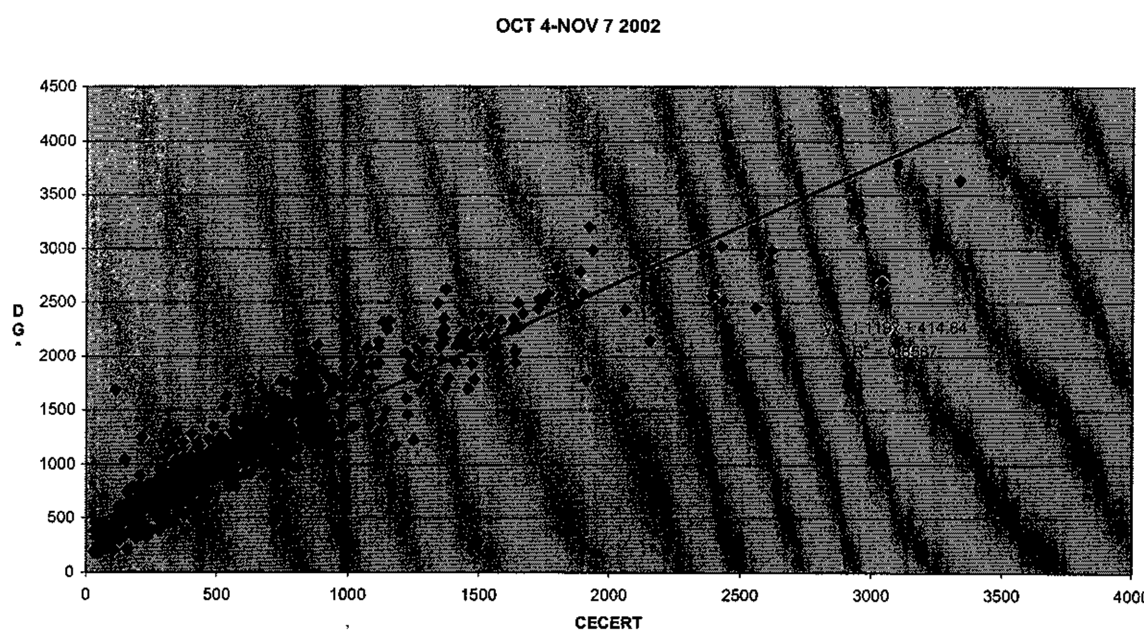

Figure 4: DGA vs. CECERT- PAN OCT4-NOV7, 2002-hourly averages

Comparison of CE-CERT and DGA data collected at Azusa essentially at the same time as this study, further demonstrates that PAN data from different instruments would have difficulty matching the strong relationship between DGA and Met Con data.

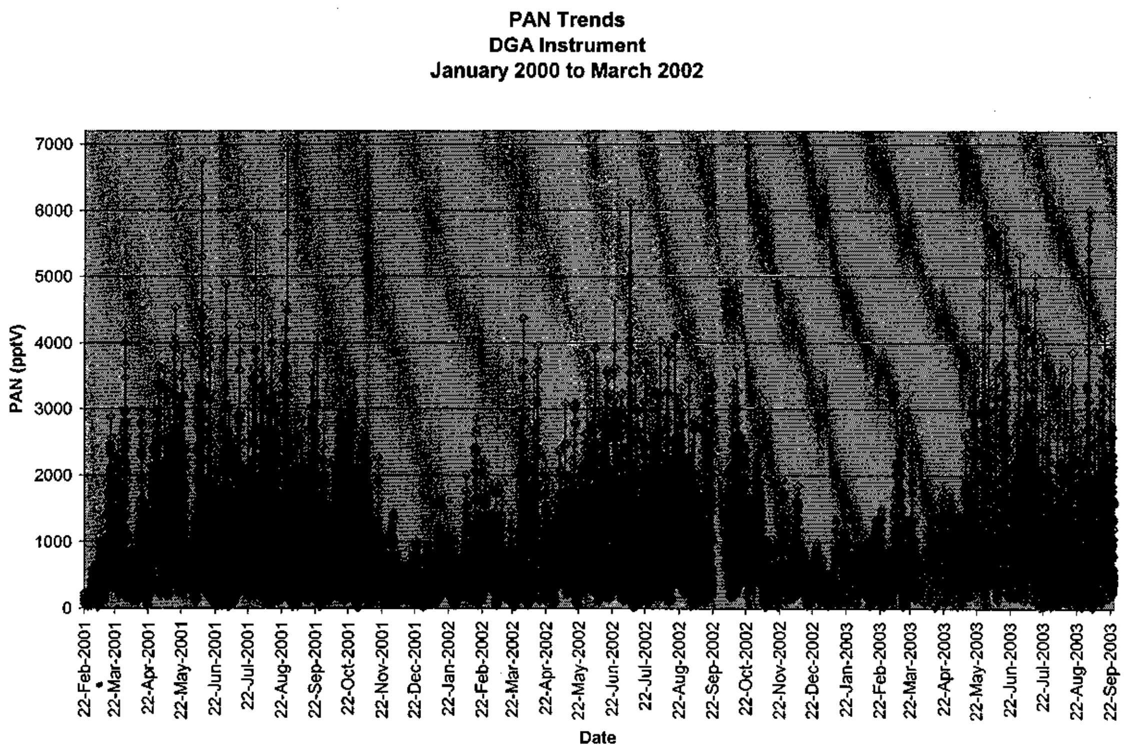

Figure 5: Entire DGA PAN Data

PAN concentrations in southern California

Table 1 has the condensed data on PAN concentrations in southern California (Grosjean, 1999) and an expansion to include the data from the most recent ARB program (date cells are shaded).

Table 1: Southern California PAN Concentrations (ppbV)			
Date	Location	Maximum	Average
Fall 87	Anaheim	19.0	
Summer 87	Anaheim	7.0	
Summer 87	Azusa	13.0	
Aug-Sep 93	Azusa	6.1	1.80
July-Oct 97	Azusa	4.8	0.88
May-Sep 00	Azusa	4.9	0.68
May-Sep 01	Azusa	7.0	1.06
May-Sep 02	Azusa	6.1	1.00
May-Sep 03	Azusa	6.0	1.02
Jan-Apr 00	Azusa	4.4	0.60
Oct 00-Apr 01	Azusa	4.2	0.47
Oct 01-Apr 02	Azusa	4.4	0.62
Oct 02-Apr 03	Azusa	3.6	0.56
Fall 87	Burbank	19.0	2.99
Summer 87	Burbank	13.0	
Jan-Apr 00	Burbank	5.4	0.56
May-Sep 00	Burbank	4.0	0.86
Oct-78	Claremont	37.0	
Aug-Sep 79	Claremont	10.0	
Sep-Oct 80	Claremont	47.0	
Summer 87	Claremont	30.0	
Sep-85	Claremont	20.0	
Sep-93	Claremont	9.9	3.00
Feb-84	Downey	7.0	
Jun-80	East Los Angeles	16.0	
Sep-90	Franklin Canyon (Santa Monica Mnt)	7.0	1.60
Aug-86	Glendora	34.0	
Fall 87	Hawthorne	16.0	
Summer 87	Long Beach	16.0	
Fall 87	Long Beach	15.0	
Aug-Sep 93	Long Beach	5.5	0.90
Sep-Nov 68	Los Angeles	65.0	
Apr-79	Los Angeles	17.0	5.00
Summer 87	Los Angeles	11.0	
Fall 87	Los Angeles	13.0	
Jul-88	Los Angeles	14.0	
Aug-Sep 88	Los Angeles	5.0	
Aug-Sep 93	Los Angeles	6.9	1.10
Sep-88	Malibu	7.0	
Sep-Oct 88	North Los Angeles	10.0	
Aug-89	North Los Angeles	8.0	

Aug-89	Palm Springs	3.0	
July-Aug 73	Pasadena	53.0	
Aug-89	Perris	7.0	
Aug-Dec 67	Riverside	58.0	5.20
Jan-Apr 68	Riverside	38.0	2.20
May-Dec 75	Riverside	25.0	3.30
Jan-Oct 76	Riverside	32.0	3.80
Jan-Apr 80	Riverside	8.0	2.30
Aug-Dec 80	Riverside	42.0	5.90
Summer 87	Rubidoux	14.0	
Aug-88	San Marino	12.0	
Summer 87	San Nicolas Island	1.0	
July-Oct 97	Simi Valley	3.0	0.60
Aug-Oct 89	Tanbark Flat (San Gabriel Mnt)	16.0	2.90
Aug-Sep 90	Tanbark Flat (San Gabriel Mnt)	22.0	4.80
Aug-91	Tanbark Flat (San Gabriel Mnt)		3.00
Jul-Aug 88	Ventura	4.0	
Aug-Sep 73	West Covina	46.0	9.40
Aug-Sep 88	West Los Angeles	10.0	
Sep-88	West Los Angeles	9.0	

A summary look at the Azusa site, with the most data available, reveals that PAN concentrations, in terms of averages, have significantly declined since late 1980's and early 1990's. However, there are still summer seasons with significant maximum concentrations (May to September 2001). Limited PAN data at Burbank also supports this view. Even so, there are not enough data from the roughly four years of measurements at Azusa to establish any unequivocal trends. Based on these limited assessment and Grosjean, D. and Grosjean E. (2005) review of their own data, trends have not yet produced clear results that would provide a guide on the effects of the "Ethanol Mandate" in southern California.

Conclusion

As noted before, the ethanol mandate was finally issued in June 2003 and probably implemented some time later. We do not know which oxygenate, if any, was used in summer 2003 gasoline formulations in southern California; although it is likely that some ethanol was used in those formulations. DGA measurements were discontinued in September 2003. There was little time to look at possible effects of the mandate. Further, we would recommend that the use of ethanol should be investigated using the acetaldehyde/formaldehyde ratio in the PAMS data. DGA investigators have had some difficulties obtaining such data. Communication of oxygenated concentration data from the AIRS network needs to be improved.

Nevertheless, the latest ARB supported PAN measurement programs are unique in providing a nearly four year stream of PAN data (2000-2003). DGA and Met Con PAN measurement methods compared very well, although we believe that

Met Con instruments may have under-reported the PAN concentrations by more than 30%. Contrasting with previous attempts to compare PAN instruments, 1993 Claremont (Los Angeles) Free Radical Study, this recent comparison was quite successful. To investigate trends, we created a continuous PAN database by combining DGA and Met Con data. Dividing the available data into Summer (May to September) and Winter (October to April), and comparing these data to the long-term record in southern California, the general downward trend in average concentrations is clear. But, high PAN episodes are still possible (2001). A preliminary investigation of the combined data does not lend support to any general trend.

References

Fitz, D. R. (2004), "Measurements of NO_Y, Nitric Acid, NO, and PAN in the South Coast Air Basin," prepared for Air Resources Board, University of California, Riverside. Contract No. 01-318.

Grosjean, D. (1983), "Distribution of atmospheric nitrogenous pollutants at a Los Angeles area smog receptor site," *Environmental Science and Technology*, Volume 17, pp 13-19.

Grosjean, D. (1999), "Ambient levels of peroxyacetyl nitrate in Southern California," prepared for Air Resources Board, DGA, Inc., August.
Met Con, Inc. (2005), AUTOMATIC PEROXYACETYL NITRATE (PAN) GC-ANALYZER, http://www.metcon-us.com/website/one_col.php?id=60

Grosjean, D. and Grosjean E. (2005), "Ambient levels of peroxyacetyl nitrate, peroxypropionyl nitrate and perchloroethylene in Azusa, CA February 2001-September 2003," Draft Final Report, Contract No. 99-703, December.

Mackay, G.I. (1994), "Los Angeles Atmospheric Free Radical Field Study: Supplementary Field Support Measurements of Formaldehyde, Hydrogen Peroxide, Nitric Acid, Nitrous Acid, Nitrogen Dioxide, Peroxy Acetyl Nitrate, NO_X, Ozone, Hydrocarbons: C_1-C_{12} and Carbonyls: C_1-Benzaldehyde Including CH_4 and CO," prepared for Air Resources Board, Unisearch Associates Inc., Contract No. 92-327.

Tuazon, E.C., Winer, A.M., and Pitts, Jr., J.N. (1981), "Trace pollutant concentrations in a multi-day smog episode in the California South Coast Air Basin by Long Path Length Fourier Transform Infrared Spectroscopy, "*Environmental Science and Technology*, Volume 15, p 1232.

AMBIENT CONCENTRATIONS OF PEROXYACETYL NITRATE (PAN), PEROXYPROPIONYL NITRATE (PPN) AND PERCHLOROETHYLENE (PCE) IN AZUSA, CA, FEBRUARY 2001 – SEPTEMBER 2003

Draft final report, December 2005

Contract 99-703, Task 3

Prepared for: **Research Division**

California Air Resources Board,

1001 I Street,

Sacramento, CA 95814

Prepared by: **Eric Grosjean and Daniel Grosjean**

DGA, Inc., 4526 Telephone Road, Suite 205

Ventura, CA 93003

Disclaimer

ACKNOWLEDGEMENTS

This work has been sponsored by the Planning and Technical Services Division and by the Research Division of the California Air Resources Board (ARB), Sacramento, CA. We thank Bart E. Croes (ARB) and Ash Lashgari (ARB) for advice and support throughout the study.

The field measurements have been carried out at the Azusa monitoring station of the South Coast Air Quality Management District (AQMD), Diamond Bar, CA. We thank John Higuchi (AQMD) for permission to carry out nearly 3 years of measurements at the site, Ken Fisher (AQMD) for keys and assistance in initial set-up, and Norman Broellos (AQMD) for logistical support and for assistance in scheduling deliveries of nitrogen cylinders.

Mr. Robert Becker (deceased) provided assistance with on-site instrument servicing, maintenance and calibrations and with data reduction. Data and other helpful information have been provided by Robert Weller (ARB, PCE data), Michael Redgrave (ARB, ozone data for 2001-2003), and Reggie Smith (ARB, PCE monitoring). We also thank Dr. James M. Roberts (NOAA Aeronomy Laboratory, Boulder, CO) for helpful input on capillary column GC analysis of PAN.

ABSTRACT

Ambient concentrations of peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and perchloroethylene (PCE) have been measured every 15 minutes in Azusa, CA, between February 2001 and September 2003. The results are discussed with focus on overall features, average seasonal and diurnal variations, short-term variations and long-term trends. Diurnal, seasonal and long-term variations of the PPN/PAN concentration ratios are also discussed, along with comparisons of the concentrations of PAN and PPN to those of ozone. Recommendations are made for future research on peroxyacyl nitrates in the atmosphere of Southern California.

TABLE OF CONTENTS

Disclaimer

Acknowledgements

Abstract

List of tables

Figure captions

1. Introduction

    1.1. Scope and deliverables for Contract 99-703

    1.2. Scope and deliverables for Task 1

    1.3. Scope and deliverables for Task 2

    1.4. Scope and deliverables for Task 3

    1.5. Additional results being made available to ARB: ambient PCE

    1.6. Contents and organization of this report

2. Experimental methods

    2.1. Overview

    2.2. Electron capture gas chromatography measurements

    2.3. Data acquisition

    2.4. Preparation of PAN and PPN standards for calibrations

    2.5. Laboratory calibrations for PAN and PPN

    2.6. Field calibrations for PAN and PPN

    2.7. Field tests of loss of PAN and PPN in the sampling line

TABLE OF CONTENTS

2.8. Field calibrations for PCE and comparison of PCE calibration standards

2.9. Heated tube tests

2.10. On-site inspection and maintenance

2.11. Other compounds observed in ambient air

3. Overview of results

3.1. Data summary, February 2001 – September 2003

3.2. Data histograms

3.3. Ambient concentrations of PAN, PPN and PCE

3.4. PPN/PAN concentration ratio

4. Seasonal and diurnal variations

4.1. Scope and contents of this section

4.2. Long-term trends

4.3. Average seasonal variations

4.4. Average diurnal variations

4.5. Comparison of PCE concentrations to those measured by ARB

5. Short-term variations

5.1. Weekdays vs. weekends

5.2. Screening of the database for short-term variations

5.3. High PCE events

5.4. High PAN and PPN concentrations outside of the smog season

TABLE OF CONTENTS (continued)

5.5. Variations of the time of maximum PAN and PPN concentrations

5.6. Other short-term variations

6. PPN/PAN concentration ratio

6.1. General considerations

6.2. Overview of results

6.3. Average seasonal variations

6.4. Average diurnal variations

6.5. Weekdays vs. weekends

6.6. Short-term variations

7. Long-term trends

7.1. Scope and contents of this section

7.2. Long-term trends for ambient PAN

7.3. Comparison of seasonal variations

7.4. Long-term trends for ambient PPN

7.5. Long-term trends for the PPN/PAN concentration ratio

8. Comparison of ambient PAN, PPN and ozone

8.1. Scope and contents of this section

8.2. Ambient ozone in Azusa, 2001 – 2003

8.3. Average diurnal variations of PAN and ozone

8.4. Concentrations of PAN vs. those of ozone measured at the same time

TABLE OF CONTENTS (continued)

8.5. Comparison of daily ozone maxima and daily PAN maxima

8.6. PAN/ozone concentration ratios

8.7. Long-term trends for ozone and PAN in Azusa

9. Summary, conclusions and recommendations

9.1. Overview of results

9.2. Average seasonal and diurnal variations

9.3. Short-term variations

9.4. PPN/PAN concentration ratio

9.5. Long-term trends

9.6. Comparison of ambient PAN, PPN and ozone

9.7. Recommendations

10. References

Appendix A. Peer-reviewed article "Peroxyacetyl nitrate and peroxypropionyl nitrate during SCOS97-NARSTO", E. Grosjean, D. Grosjean and L.F. Woodhouse, Environmental Science and Technology, 2001, 35, 4007 – 4014

Appendix B. Peer-reviewed article "Ambient PAN and PPN in Southern California from 1960 to the SCOS97-NARSTO", D. Grosjean, Atmospheric Environment, 2003, 37, Supplement S2, S221 – S238.

LIST OF TABLES

Table 2.1	PAN analyzer service and calibration logsheet
Table 3.1	Summary of ambient concentrations of PAN, PPN and PCE, Azusa, February 2001 – September 2003.
Table 4.1	High concentrations of PCE, Azusa, February 2001 – September 2003.
Table 4.2	Comparison of ambient PCE concentrations measured every 15 minutes vs. those measured by ARB in 24-hour samples.
Table 5.1	Average PAN and PCE concentrations for each day of the week in 2002 and their ratios to those measured on Sunday.
Table 6.1	Linear regression parameters for PPN vs. PAN and for PAN vs. PPN, Azusa, February 2001 – September 2003.
Table 7.1	Ambient PAN and PPN in Azusa between 1987 and 2003.

FIGURE CAPTIONS

Figure 3.1 Frequency distribution of PAN concentrations, 2003

Figure 3.2 Frequency distribution of log PAN, 2003

Figure 3.3 Frequency distribution of PCE concentrations, 2003

Figure 3.4 Frequency distribution of the PPN/PAN concentration ratio, 2003

Figure 3.5 Time series plot of ambient PAN concentrations, 2001

Figure 3.6 Time series plot of ambient PAN concentrations, 2002

Figure 3.7 Time series plot of ambient PAN concentrations, 2003

Figure 3.8 Time series plot of ambient PPN concentrations, 2001

Figure 3.9 Time series plot of ambient PPN concentrations, 2002

Figure 3.10 Time series plot of ambient PPN concentrations, 2003

Figure 3.11 Time series plot of ambient PCE concentrations, 2001

Figure 3.12 Time series plot of ambient PCE concentrations, 2002

Figure 3.13 Time series plot of ambient PCE concentrations, 2003

Figure 3.14 Time series plot of the PPN/PAN concentration ratio, 2001

Figure 3.15 Time series plot of the PPN/PAN concentration ratio, 2002

Figure 3.16 Time series plot of the PPN/PAN concentration ratio, 2003

Figure 4.1 Time series plot of monthly averaged PAN and PPN concentrations

Figure 4.2 Time series plot of maximum PAN concentration calculated from the monthly composite diurnal profiles shown in Figures 4.3, 4.4 and 4.5

Figure 4.3 Monthly composite diurnal profiles for PAN, 2001

FIGURE CAPTIONS

Figure 4.4	Monthly composite diurnal profiles for PAN, 2002
Figure 4.5	Monthly composite diurnal profiles for PAN, 2003
Figure 4.6	Monthly composite diurnal profiles for PPN, 2001
Figure 4.7	Monthly composite diurnal profiles for PPN, 2002
Figure 4.8	Monthly composite diurnal profiles for PPN, 2003
Figure 4.9	Time series plot of monthly averaged PCE concentrations
Figure 4.10	Scatterplot of monthly averaged concentrations of PCE vs. those of PAN
Figure 4.11	Time series plot of the PAN/PCE ratio of monthly averaged concentrations
Figure 4.12	Monthly composite diurnal profiles for PCE, 2001
Figure 4.13	Monthly composite diurnal profiles for PCE, 2002
Figure 4.14	Monthly composite diurnal profiles for PCE, 2003
Figure 4.15	Study-averaged composite diurnal profiles for PAN and PPN
Figure 4.16	Yearly-averaged composite diurnal profiles for PAN, 2001, 2002 and 2003
Figure 4.17	Composite diurnal profile with standard deviations for PAN, 2001
Figure 4.18	Composite diurnal profile with standard deviations for PAN, 2002
Figure 4.19	Composite diurnal profile with standard deviations for PAN, 2003
Figure 4.20	Study-averaged composite diurnal profile for PCE
Figure 4.21	Yearly-averaged composite diurnal profiles for PCE, 2001, 2002 and 2003
Figure 4.22	Composite diurnal profile for PCE, 2003
Figure 4.23	Composite diurnal profile with standard deviations for PCE, 2003

FIGURE CAPTIONS

Figure 4.24 Study-averaged composite diurnal profile for the PCE/PAN concentration ratio

Figure 4.25 Scatterplot of ambient PCE concentrations measured every 15 minutes vs. those measured by ARB in 24-hour samples

Figure 5.1 Composite diurnal profiles of PAN concentrations for each day of the week in 2002

Figure 5.2 Composite diurnal profiles of PAN concentrations for each day of the week in 2002, 9 a.m. to 5 p.m.

Figure 5.3 Composite diurnal profile of PCE concentrations for each day of the week in 2002

Figure 5.4 Time series plot of PAN minima, February 2001 – September 2002

Figure 5.5 Composite diurnal profiles of PAN minima for 2001, 2002 and 2003

Figure 5.6 Composite diurnal profiles of PCE minima for 2001, 2002 and 2003

Figure 5.7 Ambient concentration of PCE, November 29, 2001

Figure 5.8 Ambient concentration of PCE, March 30 – 31, 2001

Figure 5.9 Ambient concentration of PCE, October 26, 2001

Figure 5.10 Ambient concentration of PCE, April 29, 2001

Figure 5.11 Ambient concentrations of PAN and PPN, March 30 –31, 2001

Figure 5.12 Ambient concentrations of PAN, PPN and PCE, November 13, 2002

Figure 5.13 Composite diurnal profiles of PAN maxima for 2001, 2002 and 2003

Figure 5.14 Ambient concentrations of PAN, PPN and PCE, November 27, 2001

Figure 5.15 Ambient concentrations of PAN, PPN and PCE, December 29, 2001

Figure 5.16 Ambient concentrations of PAN, PPN and PCE, December 25 – 26, 2001

Figure 5.17 Ambient concentrations of PAN and PCE, November 25 – 28, 2002

FIGURE CAPTIONS

Figure 5.18 Ambient concentrations of PAN and PCE, December 22 – 23, 2002

Figure 5.19 Ambient concentrations of PAN and PCE, January 5 –7, 2003

Figure 5.20 Ambient concentrations of PAN, PPN and PCE, October 15 – 17, 2002

Figure 6.1 Scatterplot of log PPN vs. log PAN for all 2001 data

Figure 6.2 Scatterplot of log PPN vs. log PAN for all 2002 data

Figure 6.3 Scatterplot of log PPN vs. log PAN for all 2003 data

Figure 6.4 Histogram of PPN/PAN concentration ratios, all 2001 data

Figure 6.5 Histogram of PPN/PAN concentration ratios, all 2002 data

Figure 6.6 Histogram of PPN/PAN concentration ratios, all 2003 data

Figure 6.7 Scatterplot of monthly-averaged concentrations of PPN vs. those of PAN

Figure 6.8 Scatterplot of monthly-averaged PPN/PAN concentration ratios vs. monthly-averaged PAN concentrations

Figure 6.9 Time series plot of the slopes calculated from regression analysis of PPN vs. PAN for each month

Figure 6.10 Time series plot of the intercepts calculated from regression analysis of PAN vs. PPN for each month

Figure 6.11 Composite diurnal profile of study-averaged PPN/PAN concentration ratios shown with standard deviations

Figure 6.12 Composite diurnal profile of PPN/PAN concentration ratios, 2001

Figure 6.13 Composite diurnal profile of PPN/PAN concentration ratios, 2002

Figure 6.14 Composite diurnal profile of PPN/PAN concentration ratios, 2003

Figure 6.15 Comparison of the PPN/PAN concentration ratio composite diurnal profiles for 2001, 2002 and 2003

FIGURE CAPTIONS

Figure 6.16 Monthly-averaged CDP of the PPN/PAN concentration ratios, 2001

Figure 6.17 Monthly-averaged CDP of the PPN/PAN concentration ratios, 2002

Figure 6.18 Monthly-averaged CDP of the PPN/PAN concentration ratios, 2003

Figure 6.19 Monthly-averaged CDP of the PPN/PAN concentration ratios, July, August and September 2001

Figure 6.20 Monthly-averaged CDP of the PPN/PAN concentration ratios, June – September 2002

Figure 6.21 Monthly-averaged CDP of the PPN/PAN concentration ratios, June – September 2003

Figure 6.22 Monthly-averaged CDP of the PPN/PAN concentration ratio for June 2003, shown with standard deviations

Figure 6.23 Comparison of the CDP for the PPN/PAN concentration ratios and that for PPN concentrations, 2003

Figure 6.24 Scatterplot of PPN/PAN concentration ratios vs. PPN concentrations, 2003

Figure 6.25 Composite diurnal profiles of the PPN/PAN ratio for each day of the week in 2002

Figure 6.26 Composite diurnal profile of the PPN/PAN maxima for 2001

Figure 6.27 Composite diurnal profile of the PPN/PAN maxima for 2002

Figure 6.28 Composite diurnal profile of the PPN/PAN maxima for 2003

Figure 6.29 Composite diurnal profile of the PPN/PAN minima for 2001

Figure 6.30 Composite diurnal profile of the PPN/PAN minima for 2002

Figure 6.31 Composite diurnal profile of the PPN/PAN minima for 2003

Figure 6.32 Concentrations of PAN and PPN and PPN/PAN concentration ratio, December 28 – 29, 2001

FIGURE CAPTIONS

Figure 6.33 Concentrations of PAN and PPN and PPN/PAN concentration ratio, August 28 – 31, 2001

Figure 7.1 Peak concentrations of PAN in Southern California, 1960 - 2003

Figure 7.2 Highest 24 hour-averaged PAN concentrations in Southern California

Figure 7.3 Highest monthly-averaged PAN concentrations in Southern California

Figure 7.4 Composite diurnal profiles of ambient PAN concentrations measured in Azusa in 1987, 1993, 1997 and 2001 – 2003

Figure 7.5 Seasonal variations of peak PAN concentrations in 1967 – 68, 1975 – 76, 1980 and 2001 – 2003

Figure 7.6 Seasonal variations of monthly-averaged PAN concentrations in 1967 – 68, 1975 – 76, and 2001 – 2003

Figure 7.7 Peak PPN concentrations and highest 24 hour-averaged PPN concentrations in Southern California, 1989 - 2003

Figure 7.8 PPN/PAN ambient concentration ratio, 1989 - 2003

Figure 8.1 Time series plot of one-hour ambient ozone concentrations, Azusa, 2002

Figure 8.2 Time series plot of daily one-hour ozone maxima, Azusa, 2001 - 2003

Figure 8.3 Ozone concentrations vs. time of day, Azusa, 2002

Figure 8.4 Composite diurnal profiles for ambient PAN and ambient ozone, Azusa, 2002

Figure 8.5 Scatterplot of ambient PAN vs. ambient ozone. Azusa, 2002

Figure 8.6 Scatterplot of daily log (maximum one-hour) ozone vs. log (maximum PAN), Azusa, 2001

Figure 8.7 Time series plots of daily maximum one-hour ozone and daily maximum PAN concentrations, Azusa, 2001

FIGURE CAPTIONS

Figure 8.8	Time series log plots of daily maximum one-hour ozone and daily maximum PAN concentrations, Azusa, 2001
Figure 8.9	Scatterplot of daily maximum PAN vs. daily maximum one-hour ozone, Azusa, 2001
Figure 8.10	Time series plot of the PAN/ozone ambient concentration ratio, Azusa, 2002
Figure 8.11	Diurnal variations of the PAN/ozone ambient concentration ratio, July 7, 2002
Figure 8.12	Diurnal variations of the PAN/ozone ambient concentrations ratio, August 30 – 31, 2002
Figure 8.13	Diurnal variations of the PAN/ozone ambient concentration ratio, March 23 – 24, 2002
Figure 8.14	Plot of the PAN/ozone ambient concentration ratio vs. time of day, Azusa, 2002
Figure 8.15	Composite diurnal profiles of the PAN/ozone and PPN/ozone ambient concentration ratios, Azusa, 2002
Figure 8.16	Long-term trends in highest one-hour ozone and highest PAN concentrations, Azusa, 1980 – 2003

1. INTRODUCTION

1.1 Scope and deliverables for Contract 99-703

Contract 99-703 consists of three tasks:

Task 1. Reduction and reporting of SCOS97-NARSTO PAN data

Task 2. Descriptive analysis of PAN trends in southern California

Task 3. Measurements of PAN and PPN at two southern California locations

Task 1 and Task 2 have been completed, and Task 3 is described in the present report. Brief descriptions of the scopes and deliverables for each Task are given below.

1.2 Scope and deliverables for Task 1

Task 1 involved the reporting of ambient concentrations of PAN measured during SCOS97-NARSTO, which was carried out during summer 1997. As part of SCOS97-NARSTO, we measured ambient concentrations of PAN at two locations, Azusa and Simi Valley. Monitoring of ambient PAN was carried out for ca. four months in Azusa (June 12 – October 16, 1997) and for about three months in Simi Valley (July 16 – October 16, 1997). Under subcontract 98-02 to CE-CERT, University of California, Riverside, and as part of CE-CERT's ARB Contract 96-540, we had previously reported ambient concentrations of PAN and PPN in Azusa and Simi Valley for the 17 days selected by ARB for intensive measurements, called IOP days (13 IOP days and 4 aerosol IOP days). The objective of Task 1 was to report all PAN data for the 4 months of measurements in Azusa and for the 3 months of measurements in Simi Valley. The deliverable for Task 1, as requested by ARB, consisted of a spreadsheet submitted in electronic form and that contained the following entries: location (Azusa or Simi Valley), date, time of measurement (PST) and concentrations of PAN (units: ppb).

At the completion of Task 1, we carried out a descriptive analysis of the results obtained during SCOS97-NARSTO and carried out calculations of the loss of PAN due to thermal decomposition. This work was published in a peer-reviewed article entitled "Peroxyacetyl nitrate and peroxypropionyl nitrate during SCOS97-NARSTO" (E. Grosjean, D. Grosjean and L.F. Woodhouse, Environmental Science and Technology, 2001, Volume 35, pp. 4007 – 4014). A copy of this article is included as Appendix A.

1.3 Scope and deliverables for Task 2

The scope of Task 2 was to review, organize and analyze the historical data for ambient levels of PAN in southern California, from the earliest studies carried out in the 1960s to the most recent body of data, i.e., that for SCOS97-NARSTO being reported as Task 1 of the present contract. This review of 35 studies spanning 37 years included the following topics: long-term trends in ambient levels of PAN in southern California, highest PAN concentrations, time-averaged PAN concentrations, diurnal variations, seasonal variations, spatial variations, thermal decomposition of PAN, ambient levels of PPN, PPN/PAN ambient concentration ratios, and long-term trends in the PPN/PAN and PAN/ozone concentration ratios. The deliverable for Task 2, as requested by ARB, was a stand-alone report, whose results and conclusions were used as input by ARB in the context of assessing the possible impact, on future ambient air quality, of replacing MTBE by ethanol in gasolines sold in California. The report was subsequently published as a peer-reviewed article entitled "Ambient PAN and PPN in southern California from 1960 to the SCOS97-NARSTO" (D. Grosjean, Atmospheric Environment, 2003, Volume 37, pp S221 – S238) in the special issue of Atmospheric Environment devoted to SCOS97-NARSTO and dedicated to Professor Glen R. Cass. A copy of this article is included as Appendix B.

1.4 Scope and deliverables for Task 3

The scope of Task 3 involved long-term measurements of ambient PAN and ambient PPN in southern California. Task 3 has been carried out under Contract 99-703 and subsequently under a Memorandum of Understanding dated March 20, 2002. The scope of Task 3, which initially called for measurements to be made at two locations, was subsequently modified to allow for measurements to be made over a longer period but at only one location, Azusa. Thus, PAN and PPN have been measured in Azusa every ca. 15 minutes from February 2001 to September 2003. The corresponding results, which are described in the present report, constitute the longest continuous study of ambient PAN and ambient PPN in southern California, where PAN was first identified and measured in ambient air in 1960 (Grosjean, 2003).

Deliverables for Task 3 are as follows:

Three (3) CD-ROM have been previously submitted to ARB, one in November 2004 with all 2001 data, one in January 2005 with all 2002 data, and one in June 2005 with all 2003 data. Each CD-ROM included worksheets in Microsoft EXCEL 2000 for PC. The worksheets included, for each month, the date, time (PST) and ambient concentrations of PAN, PPN, and PCE (see section 1.5 below) measured every 15 minutes. Additional worksheets were included to present data summaries. The CD-ROM that included the 2001 data and 2002 data also included graphs such as time series plots of PAN, PPN and PCE concentrations, composite diurnal profiles of concentrations averaged over one-month periods, scatterplots of PPN vs. PAN and PAN vs. PCE, and plots of the PPN/PAN ambient concentration ratio. A list of all worksheets and graphs was included at the beginning of each CD-ROM.

The final deliverable for Task 3 is the present report, whose contents and organization are described in section 1.6.

1.5 Additional results being made available to ARB: ambient PCE

We measured PAN and PPN by electron capture gas chromatography, see section 2 below. The experimental conditions we selected to measure ambient PAN and PPN also yielded information on other compounds present in ambient air. One of these compounds is perchloroethylene (PCE, tetrachloroethylene). We also used PCE as a standard as part of our protocol for quantitative analysis and calibrations, and therefore the concentrations of PCE present in ambient air could be readily measured.

We elected to measure and report ambient PCE along with ambient PAN and PPN. The PCE database consists of ca. 90,000 measurements made in Azusa every 15 minutes between February 2001 and September 2003. The PCE data and the corresponding data interpretation and descriptive analysis are made available to ARB at no cost. ARB measures toxic air contaminants, including PCE, at many locations where samples of 24-hour duration are collected every 12 days. Thus, our results for PCE in Azusa complement those of the ARB monitoring program and offer opportunities to examine short-term variations of ambient PCE over a period of ca. 31 months at a southern California location. Detailed information on ambient PCE is of interest in the context of several research and regulatory issues. For example, detailed information on ambient PCE may be used to measure the success of regulatory programs aimed at reducing PCE emissions by phasing out the use of PCE in dry cleaning, degreasing, and other activities.

1.6 Contents and organization of this report

The report is divided into nine sections that describe our measurement and calibration protocols (section 2) and that present descriptive analysis of the results (sections 3 – 9). Section 3 gives an overview of the results. Average seasonal and diurnal variations are discussed in section 4, and short-term variations (including weekdays vs. weekends) are described in section 5. Section 6 focuses on the PPN/PAN ambient concentration ratio and its average and short-term variations. Section 7 examines long-term variations of PAN and PPN in southern California, and section 8 compares variations of PAN and PPN to those of ozone. Summary, conclusions and recommendations are outlined in section 9, and references are listed in section 10. The two peer-reviewed articles that describe work carried out in Task 1 and Task 2 are included as Appendix A and Appendix B, respectively.

2. EXPERIMENTAL METHODS

2.1 Overview

Measurements of PAN, PPN and PCE in ambient air were made at the South Coast Air Quality Management District (SCAQMD) air monitoring station located at 803 Loren Avenue in Azusa, CA (latitude N 34:08:09, longitude W 117:55:22, California Air Resources Board location code 2484). Measurements of ambient PAN, PPN and PCE were made from February 22, 2001 to September 24, 2003. The measurement and calibration protocols are described in Sections 2.2 to 2.10 below. These sections focus on electron capture gas chromatography measurements, data acquisition, preparation of PAN and PPN standards, PAN and PPN calibrations in the laboratory, PAN and PPN calibrations at the field location, field tests of loss of PAN and PPN in the sampling line, calibrations for PCE, heated tube tests, and on-site inspection and maintenance. Other compounds observed in ambient air along with PAN, PPN and PCE are briefly discussed in Section 2.11.

2.2 Electron capture gas chromatography measurements

Ambient levels of PAN and PPN were measured by electron capture gas chromatography using a Scientific Research Instruments model 8610C gas chromatograph (GC) and a Valco model 140 BN electron capture detector (ECD). The new GC was configured with a 10-port electrically operated Valco gas sampling valve with a 1cc stainless steel sampling loop, EPC (electronic pressure control) of carrier gases, a thermostatted valve oven, an 8 position relay board to electronically control external components such as solenoid valves, and a programmable vacuum pump interface to control the on and off cycles of the pump. We used a KNF model UN86KTI pump with Viton heads, Viton valve seals and a Teflon coated diaphragm to draw the sample through the sampling line at ~ 375 cc/min.

The measurement protocol was similar to that described previously (Grosjean, et al, 1996, 2001) except that capillary columns were used instead of packed columns. The capillary column was an Rtx 200-MS, 15 meter long by 0.53mm i.d. and 1 μm phase thickness. The operating conditions were: column oven temperature 30C, valve oven temperature 30C, ECD cell temperature 60C, ECD current 800 mV, UHP N_2 regulator pressure 30 psig, carrier gas setting 5 units, column flow 16.4 cc/min, ECD makeup flow 40.0 cc/min, and total flow 56.4 cc/min. The carrier gas was UHP nitrogen passed through a UOP N_2 purifier that was changed every four cylinders or more often if contamination was suspected. The sampling line was made of ~ 20 feet of ¼" OD (5/32" ID) PFA Teflon tubing and was routed to the roof of the building on a mast ~ 3 feet above the roof. A 47mm Teflon filter holder that contained a 5 μm Teflon filter was placed at the sampling line inlet to prevent contamination by particles. The filter was changed weekly or more often if it appeared dirty visually. The sampling frequency was 15 minutes, which was more than sufficient for later peaks to elute and to obtain a clean baseline at the start of the next chromatogram.

The retention times were 1.39 ± 0.01 min for PCE, 1.76 ± 0.01 min for PAN, and 3.27 ± 0.02 min for PPN over the course of the study. To examine the possibility of other compounds co-eluting with PCE, PAN, or PPN, we injected ~10 ppbv standards of several chlorinated hydrocarbons and organic nitrates that have been shown in previous work to have a significant response on the GC-ECD. Methyl nitrate eluted at 0.683 min, trichloroethylene at 0.783 min, ethyl nitrate at 1.15 min, n-propyl nitrate at 2.03 min, and n-butyl nitrate at 4.983 min. These compounds did not interfere with the measurement of PCE, PAN, or PPN. In addition, there was a small peak that eluted around 1.10 min and that was either column bleed, water, or both.

2.3 Data acquisition

The Peak Simple software was used to load the valve for 2 minutes and then switch to the "inject" position at which point the baseline was adjusted to zero. The chromatogram was stopped at 14.80 minutes, and 0.20 minutes were used to save the data files before the next injection. The sampling rate was 1Hz. We found that sampling at higher frequencies resulted in higher noise with no gain in detection limits. Data files were saved automatically and were backed up on a second hard drive nightly and on CDs weekly on the computer that controlled the GC via the Peak Simple software. Data were also viewed remotely using a dedicated phone line, PCanywhere (Symantec Corp.) software, and dial up modems that allowed us to examine the current chromatogram on a real-time basis and to examine older chromatograms as well. The data files were integrated automatically using Peak Simple and various integration settings and were converted to Excel 2000 files for PC. Due to the large oxygen peak that elutes at the start of the chromatogram and the resulting variation in the baseline "recovering" from this peak, ca. 15 % of the chromatograms contained one or more peaks that had to be reintegrated manually. These peaks were either very small, i.e. near the detection limit, or occurred after there was an abrupt change in the baseline. As part of quality assurance, we manually integrated and visually inspected one out of every 30 files and compared the peak areas and sampling times to those of the auto-integrated data.

2.4 Preparation of PAN and PPN standards for calibrations

Small amounts (~50ml) of PAN and PPN were synthesized as needed (~monthly) in the liquid phase using dodecane as the solvent and were stored in 20 ml glass vials with Teflon lined caps in a freezer. For each calibration, a vial was partially thawed and, using a 5ml Teflon coated glass syringe, several ml of the headspace above the vial were injected into 50.0 L Teflon FEP sampling bags with on/off valves. To prevent any nitric acid left over from the synthesis from entering the syringe, we placed a small plug of nylon made from 25 mm nylon filters at the tip of the syringe inside a small piece of PFA Teflon tubing. The Teflon bag was then filled to almost full with purified air produced by a custom-built pure air generator that uses cartridges containing silica gel, activated carbon and Purafil to remove impurities from compressed ambient air. The purified air thus obtained contained less than 0.1 ppbv NO_X. The humidity was kept at ca. 55% to help condition the surface of the Teflon bag. A 1 μm cartridge filter followed by several Teflon and nylon filters inside a 47mm Teflon PFA filter holder were used to remove any particles and nitric acid from the air stream before it passed to the main flow meters where the airstream was split into several smaller streams. The pure air generator cartridges were replaced when NO_X levels exceeded 0.2 ppbv or were not constant over a period of an hour.

2.5 Laboratory calibrations for PAN and PPN

We used two API 200A NO_X analyzers to measure PAN and PPN in the Teflon bags after measuring the levels of NO_X in another Teflon bag (control bag) filled with the same purified air as that used to fill the bags that contained PAN and PPN. Each bag was sampled for ~ 10 minutes or until a steady value of NO_X was obtained for more than 5 minutes. Typical values were around 10 ppbv after subtracting the background value of ca. 0.1 ppbv. The NO_X analyzers were calibrated on the same day the PAN calibrations were carried out using an API 700 calibrator and a Scott-Marrin cylinder of NO in N_2 certified at 49.9 ppm ± 1% (cylinder No. CA02559, traceable to NIST reference standard SRM 1683b). The two NO_X analyzers were inspected and serviced on a weekly basis including changing the Teflon particulate filter and performing a checklist of various instrument parameters. To assess if there was any nitric acid in the PAN and PPN standards, we inserted a 47mm Teflon filter holder containing three 47mm nylon filters in line to the NO_X analyzer and measured any change in the response of the NO_X analyzer. These tests were repeated every time a new batch of PAN or PPN was prepared. The tests always gave the same results with or without the nylon filters, indicating that no nitric acid was present in any of the PAN and PPN standards. The nylon filters were replaced with a short piece of Teflon tubing loosely packed with nylon wool and the same results were obtained in two separate tests. We also checked the conversion efficiency of the NO_X analyzer for PAN and PPN by decomposing PAN and PPN to NO_2 using a short piece of FEP Teflon tubing heated to ~170°C and measuring the concentration change, if any, using the NO_X analyzer. We performed 22 converter efficiency tests for both PAN and PPN and the concentrations were always the same as those measured without the heated tube to within 0.1 ppbv. We initially calibrated the PAN analyzer in the laboratory on a daily basis for 2 weeks with 5 points at ~ 1,3,6,12, and 25 ppbv, along with a zero point, and found the analyzer to be linear for the full range used (R^2 =0.9999) and to not deviate by more than 3% at any of the 5 points over the 2 week period.

Several chemically coated filters and ozone removal devices were tested for their potential to selectively remove PAN from ambient air. All tests were carried out at PAN concentrations of 10-15 ppbv. The results of these tests indicate that NaCl-coated filters typically used to remove HNO_3 do not remove more than 5% of PAN; that KI scrubbers typically used to remove ozone remove ~33% of PAN; that ozone scrubbers taken from Dasibi ozone analyzers remove ~80% of PAN, and that KOH-coated filters remove ~60% of PAN.

2.6 Field calibrations for PAN and PPN

As soon as the PAN and PPN measurements were completed in the laboratory, the 3 Teflon bags containing PAN, PPN and purified air were placed in a custom-built thermoplastic-foam insulated dark plastic container filled with dry ice/blue ice and were taken to the field site for analysis. We calibrated the field analyzer for PAN and PPN on a weekly basis with a ~10 ppbv standard and every other week with ca. 2 ppbv and ca. 10 ppbv standards. About once a month we performed a 3-point calibration of 2, 10, and 25 ppbv with PAN or PPN. There were no major differences in the response factors from any of the 3 points, except on one occasion when the low point was slightly off due to the additional uncertainties in the NO_X measurement at that low value. The analyzer was calibrated by first making 2-3 injections from the Teflon bag that contained purified air, followed by 5-7 injections from each of the PAN and PPN bags and then flushed with another 2-3 injections from the bag that contained only purified air. The analysis was performed for logistical purposes indoors (using a tee in the sampling line), where we could keep the bags near the output of the air conditioning unit mounted in the wall near the PAN analyzer.

2.7 Field tests of loss of PAN and PPN in the sampling line

To assess losses through the Teflon filter and the sampling line used to sample ambient air, we performed calibrations on the roof at the inlet of the line on a ~ monthly basis at night or in the early morning when the temperature was low. The "roof" measurement protocol consisted of first making a set of indoor measurements followed by a set of roof measurements and then another set of indoor measurements. The PAN and PPN measurements at the roof inlet were typically 1.5% lower than those measured indoors after subtracting the PAN or PPN lost while performing the roof calibrations. Typical loss rates in the bags were about the same for PAN and PPN. They ranged from 0.4 to 1.5% per hour while calibrating indoors and from 1.2% to 3.6% per hour while calibrating on the roof.

To assess the stability of PAN and PPN in the cooled containers used to transport the bags to the field we made several measurements from each bag, returned them to the storage containers, left them in the transport vehicle for the same time as the typical transport time from our laboratory to the field location (~70 minutes), and then reanalyzed them for PAN and PPN. The resulting losses were 0.8-1.5% per hour for both PAN and PPN (n=5).

To confirm that there were no other co-eluting peaks in the PAN and PPN standards, each calibration sample (weekly) was passed through a short piece of heated Teflon FEP tube maintained at ~165°C for 1-3 injections with resulting losses of >99% for both PAN and PPN in all samples. Upon return to the laboratory the PAN and PPN standards were reanalyzed with the NO_X analyzer. The resulting NO_X loss rates were ~ 1% per hour, i.e. these loss rates were similar to those measured on-site with the GC-ECD. The calibrations yielded response factors (peak height, mv/ppbv) of 60.9 ± 4.9 for PAN and 39.6 ± 4.0 for PPN. The response factors for peak area/ppbv were quite similar, i.e. 427.4 for PAN and 450.6 for PPN, resulting in a PPN/PAN peak area response factor ratio of 1.053. There was no trend in either PAN or PPN response factors over the duration of the study (ca. 32 months). The overall uncertainty in the PAN and PPN measurements was ± (3ppt +15%).

2.8 Field calibrations for PCE and comparison of PCE calibration standards

Two primary standards (±5%) of PCE in N_2 at 2000 psig contained in aluminum cylinders fitted with brass valves were obtained from Scott-Marrin Inc. at concentrations of 4.96 and 4.41 ppbv (cylinders No. CC72111 and JJ18969). The GC-ECD was calibrated 4 times with 7 PCE concentrations ranging from 0.1 to 4.96 ppbv obtained by dilution using an Environics Model 100 calibrator. The response was found to be linear (R^2 > 0.9999) for the full range tested. Beginning on July 14, 2001, the GC-ECD was calibrated for PCE by making 5-7 injections of the 4.96 or 4.41 ppbv standard. These calibrations were carried out at least once a week and every time PAN and PPN calibrations were performed.

The PCE calibrations yielded PCE response factors (peak height, mv/ppbv) of 100.2 ± 3.3 for the duration of the study (n=91, data for weekly calibrations carried out along with those for PAN and PPN). The overall uncertainty in the PCE measurements was ± (2ppt +15%). The PCE response factor for the 4.96 ppbv standard decreased by ~0.3% per month in the ~25 month period during which weekly PCE calibrations were performed.

We compared the 4.96 ppbv (standard A) and 4.41 ppbv (standard B) standards 6 times between 9/22/2001 and 7/3/2003. The average B/A ratio of the peak height response factors was 1.085 ± 0.005. The data suggest a slight trend of decreasing B/A ratio over time, at ~ 0.12% per month over the 25-month period. The average B/A ratio lies within the combined uncertainties of the two standards (± 5%), along with the associated analytical uncertainties of the GC-ECD. It is likely that some of the decrease in the PCE response factor over time was due to loss of PCE in the aluminum cylinder and not to changes in the response of the GC-ECD.

2.9 Heated tube tests

We performed heated tube tests on ambient air samples to verify that the peaks we identified as PAN and PPN decomposed and that PCE did not. These tests were performed at least weekly by bracketing a heated tube test between 2 injections of ambient air and by calculating the percent change as [(PAN initial-PAN final)/2 -PAN (heated tube)] / (PAN initial-PAN final)/2)*100. The results were 0-1% removal for PCE and 85-99% removal for PAN and PPN.

2.10 On-site inspection and maintenance

The operating conditions of the instrument were verified remotely several times every week using the PCanywhere software to check that the retention times were correct and that the files were generated in proper order and with the correct time. On-site inspections of the GC-ECD were performed weekly and involved a visual inspection of the analyzer and sampling line, changing the Teflon filter, recording a checklist of instrument parameters, backing up the files to CDs, and changing N_2 cylinders and N_2 purifiers as needed. The sampling pump was rebuilt or replaced about every 6-12 months. All relevant information gathered during the weekly on-site inspections was compiled on spreadsheets, an example of which is given in Table 2.1.

2.11 Other compounds observed in ambient air

Compounds that eluted after 5 minutes are not discussed in this report, but at least 7 other peaks were identified on days of high ambient PAN concentrations. It is likely that at least 3 of these peaks were peroxyacyl nitrates since these peaks decomposed when the sample was heated to ~160°C. There was also one PAN-type compound, most likely APAN, present in the chromatograms on days when PAN was high. The peak tentatively attributed to APAN eluted between PAN and PPN.

3. OVERVIEW OF RESULTS

3.1 Data summary, February 2001 – September 2003

PAN, PPN and PCE have been measured in Azusa every 15 minutes from February 2001 to September 2003, thus yielding ca. 90,000 valid measurements of the ambient concentrations of PAN, PPN and PCE. An overview of the results is given in Table 3.1.

Table 3.1 summarizes the results according to calendar month. For each month, the table includes the following entries: PCE, PAN and PPN monthly average concentrations, in units of ppbv (AVERAGE), the corresponding standard deviations (STDEV) and percent relative standard deviations (RSD %), the lowest (MIN) and highest (MAX) concentrations measured during the month, the number of valid measurements during the month (COUNT), the number of 15 minute periods in the month (TOTAL # of 15 MIN) and the percent data capture (% DATA CAPTURE), i.e., the ratio COUNT/TOTAL # of 15 MIN. Also included in Table 3.1 for each month are the PPN/PAN and PCE/PAN concentration ratios.

The last three columns in Table 3.1 (AVE, MIN and MAX) give a summary of data for the entire study. The column AVE gives an average of all monthly averages for the following parameters: concentrations of PCE, PAN and PPN, percent data capture for PCE, PAN and PPN, and PPN/PAN concentration ratios. The columns MIN and MAX give the lowest and highest values measured or calculated for the following parameters: monthly averaged concentrations (PCE, PAN, PPN) and concentration ratio (PPN/PAN) monthly average percent data capture (PCE, PAN and PPN), and lowest and highest concentrations (PCE, PAN and PPN) and concentration ratio (PPN/PAN) measured in a given month. For example, the column AVE in Table 3.1 indicates that the averages of all monthly averages were 0.172 ppb for PCE, 0.790 ppb for PAN, 0.091 ppb for PPN, 0.113 for the PPN/PAN concentration ratio, and 96.7 percent for data capture. The column MAX in Table 3.1 indicates that the highest concentrations measured from February 2001 to September 2003 were 33.15 ppb for PCE, 7.39 ppb for PAN and 0.97 ppb for PPN.

As mentioned in section 2 above, the limits of detection (LD) were 1 ppt for PCE, 1.7 ppt for PAN and 1.15 ppt for PPN (1 ppt = 10^{-3} ppb). The column MIN in Table 3.1 indicates that the lowest concentrations measured were 7 ppt for PCE, 15 ppt for PAN, and 2 ppt for PPN (rounded off from 1.7 ppt for clarity). Thus, PCE, PAN and PPN could be measured in all of the ca. 90,000 valid chromatograms obtained during the study. The ratios of lowest concentrations measured/limit of detection were 7.0 for PCE, 8.8 for PAN and 1.5 for PPN, i.e., for PPN the lowest concentrations measured were near our limit of detection.

Data capture averaged 96.7 percent, was 97 – 100 percent for all but five months, was 95 percent in May 2002 and September 2003, and was 83, 69 and 88 percent in May 2001, September 2002 and October 2002, respectively. Factors that contributed to less than optimal data capture included instrumental, data acquisition, and/or logistical problems, such as the failure of the air conditioning system.

3.2 Data histograms

Because of the large number of measurements, a statistical analysis of the overall features of the database was deemed appropriate. We constructed histograms (frequency distribution plots) of concentrations of PAN, PPN and PCE and of the PPN/PAN concentration ratio. As an example, Figure 3.1 shows the histogram of PAN concentrations measured in 2003 (ca. 25,200 measurements; data for PAN in 2001 and 2002 and data for PPN, not shown, exhibited the same features as those shown in Figure 3.1). The frequency distribution plot shown in Figure 3.1 is indicative of a lognormal distribution. The corresponding frequency plot for log PAN in 2003 is shown in Figure 3.2. Concentrations of PCE also exhibited a log normal distribution. This is illustrated in Figure 3.3, which shows a frequency plot of log PCE for 2003. Figure 3.4 shows that the PPN/PAN concentration ratios exhibited a normal distribution centered at ca. 0.12. A more detailed analysis of PPN/PAN concentration ratios is given in Section 6.

3.3 Ambient concentrations of PAN, PPN and PCE

Ambient concentrations of PAN, PPN and PCE have been measured in Azusa from February 2001 to September 2003. Concentrations measured every 15 minutes (ca. 89,000 entries) are listed in the CD-ROM previously submitted to ARB. The figures presented in this section are examples of time series plots of ambient concentrations. They are intended to illustrate the overall features of the large set of measurements made in this study. Seasonal and diurnal variations of the ambient concentrations of PAN, PPN and PCE are discussed in more detail in section 4.

Time series plots of ambient PAN concentrations are shown in Figure 3.5 (2001), Figure 3.6 (2002) and Figure 3.7 (2003). Ambient concentrations of PAN ranged from 0.015 ppb (15 ppt) to ca. 7 ppb. The highest PAN concentrations measured were 7.39 ppb in 2001, 6.39 ppb in 2002 and 6.50 ppb in 2003. Time series plots of ambient PPN concentrations are shown in Figure 3.8 (2001), Figure 3.9 (2002) and Figure 3.10 (2003). Ambient concentrations of PPN ranged from 0.002 ppb (2 ppt) to ca. 1.0 ppb. The highest PPN concentrations measured were 0.97 ppb in 2001, 0.83 ppb in 2002 and 0.86 ppb in 2003. Variations in ambient concentrations of PPN were generally (but not always, see section 6) similar to those of PAN. In particular, there was an increase in the frequency of days with higher concentrations of PAN and PPN from mid-spring to early fall.

Time series plots of ambient PCE concentrations are shown in Figure 3.11 (2001), 3.12 (2002) and 3.13 (2003). Ambient concentrations of PCE ranged from 0.007 ppb (7 ppt) to 33.15 ppb in 2001, 22.56 ppb in 2002 and 10.87 ppb in 2003. The overall features of the PCE database are different from those for PAN and PPN with respect to diurnal, seasonal and long-term variations. Ambient PCE generally ranged up to 2 ppb, with occurrences of much higher concentrations that were recorded in winter, spring and fall but not during summer. The number of occurrences of high PCE concentrations and the corresponding concentrations were lower in 2002 than in 2001 and again lower in 2003 than in 2002.

3.4 Ambient PPN/PAN concentration ratio

The PPN/PAN ambient concentration ratios are shown in the time series plots given in Figure 3.14 (2001), Figure 3.15 (2002) and Figure 3.16 (2003). Many of the ratios were within a somewhat narrow range, ca. 0.09 – 0.14 (the monthly averages given in Table 3.1 ranged from 0.095 to 0. 124 and averaged 0.113). There were occurrences of higher PPN/PAN concentration ratios (as high as 0.42, e.g., in February, September and December 2001) as well as occurrences of lower PPN/PAN concentration ratios (as low as 0.026, e.g., in September 2001, August 2002 and January and August 2003). The PPN/PAN ambient concentration ratio and its seasonal and diurnal variations are analyzed in more detail in section 6.

4. AVERAGE SEASONAL AND DIURNAL VARIATIONS

4.1 Scope and contents of this section

The time series plots shown in section 3 for all individual measurements indicate that ambient concentrations of PAN, PPN and PCE exhibit temporal variations on several time scales. We examine in this section long-term variations, average seasonal variations and average diurnal variations. Short-term variations are discussed in section 5.

Long-term variations are examined in section 4.2 below for the study period, February 2001 – September 2003. Longer-term variations of PAN and PPN are discussed in section 7, in which data from this study are compared to historical data, i.e., ambient levels measured in southern California since 1960.

Average seasonal variations are discussed in section 4.3. These seasonal variations are illustrated by plots of monthly-averaged concentrations and by plots of monthly-averaged composite diurnal profiles (CDP). Average diurnal variations are discussed in section 4.4 and are illustrated by plots of CDP averaged over one month, one year, and/or the entire study.

Average seasonal and diurnal variations discussed in this section are those of ambient concentrations of PAN, PPN and PCE. The PPN/PAN ambient concentration ratio and its temporal variations are described in section 6 and are compared to historical data in section 7.

4.2 Long-term trends

For PAN and PPN, the time series plots of individual data shown in section 3 and the corresponding monthly averaged concentrations (Table 3.1) give no indications of a long-term trend between February 2001 and September 2003. In contrast, the time series plots of individual data shown in section 3 for PCE indicate that the frequency of occurrence of high PCE concentrations decreased from 2001 to 2002, and again from 2002 to 2003. A list of the days and times high PCE concentrations were recorded is given in Table 4.1. Table 4.1 indicates that ambient PCE exceeded 2.0 ppb 150 times on 42 days in 2001, 35 times on 20 days in 2002, and 18 times on 15 days in 2003. Table 4.1 also indicates that high PCE events also decreased in magnitude from 2001 to 2003. For example, the highest PCE concentrations recorded were ca. 33 ppb in 2001, 23 ppb in 2002, and 11 ppb in 2003.

4.3 Average seasonal variations

On average, ambient concentrations of PAN and PPN increased from winter to summer. This is shown in Figure 4.1, which is a times series plot of the monthly-averaged PAN and PPN concentrations (see Table 3.1). This is also shown in Figure 4.2, which is a time series plot of the maximum PAN concentration calculated from monthly composite diurnal profiles (CDP), i.e., CDP plots of PAN (or PPN) concentration vs. time of day for each month of the study. These monthly CDP plots are shown in Figure 4.3 (PAN, 2001), Figure 4.4 (PAN, 2002), Figure 4.5 (PAN, 2003), Figure 4.6 (PPN, 2001), Figure 4.7 (PPN, 2002) and Figure 4.8 (PPN, 2003). These CDP plots all show a trend for daytime PAN and PPN maxima to be higher, on average, during summer.

On average, and with the caveat that PCE averages are influenced by infrequent events of high concentrations, ambient concentrations of PCE were higher in winter. A time series plot of monthly-averaged PCE concentrations is shown in Figure 4.9. The number and the magnitude of high PCE events decreased from 2001 to 2003, (see Table 4.1 above), and as a result monthly averaged concentrations also decreased.

PCE is a primary pollutant, is emitted mostly by stationary sources, and is essentially unreactive in urban air. PAN and PPN are secondary pollutants, i.e., they have no direct sources and are formed in-situ in photochemical reactions involving volatile organic compounds (VOC) and oxides of nitrogen. Vehicle emissions are a major source of the VOC that are precursors to PAN and PPN. Thus, seasonal variations of PCE are expected to be approximately in the opposite direction of those of PAN and PPN. Indeed, Figure 4.10 shows little or no association (R^2 = 0.05) between monthly averaged PCE concentrations and monthly averaged PAN concentrations, and Figure 4.11 shows that the ratio PAN/PCE of monthly averages increases from winter to summer (and also from 2001 to 2003, consistent with the overall decrease in ambient PCE, but not in ambient PAN or PPN, during the study period).

The three plots shown in Figure 4.12 (2001), Figure 4.13 (2002) and Figure 4.14 (2003) are monthly CDP of ambient PCE. They illustrate that caution must be exercised when describing average seasonal (see above) and diurnal variations of PCE in Azusa. In 2001, there was a higher frequency of events with high PCE concentrations, and Figure 4.12 shows which monthly averages were most affected, in this case March, October and April. Figure 4.12 also shows that monthly averages were affected at different time of day, i.e., at night in March, in the morning in October, and in the afternoon and evening in April. Fewer high PCE events were recorded in

2002, and Figure 4.13 shows that they contributed to monthly averaged values mainly in February and during the early morning hours. Figure 4.14 shows that in 2003, during which the frequency and magnitude of high PCE events were lowest, these events affected monthly averages in winter (January and September) and this in the morning hours.

The high PCE events recorded throughout the study may be indicative of PCE emissions near our sampling location. Indeed, the ARB web site indicates that one of the major stationary sources of PCE in southern California is close to our sampling location, and that there are other smaller sources nearby. High PCE events may also result from transport of PCE emitted upwind and there are numerous point sources of PCE in the region. Further analysis of the data, perhaps including an examination of PCE/tracer concentration ratios (e.g., PAN, CO, toxics other than PCE, etc.) together with prevailing meteorology, may indicate the relative contribution of nearby and more distant sources to ambient PCE concentrations measured in Azusa.

4.4 Average diurnal variations

On average, diurnal variations of PAN and PPN included a gradual increase from early morning to early afternoon followed by a gradual decrease from early afternoon to early morning. These diurnal variations have been recorded many times in earlier studies of ambient PAN and PPN in southern California and are shown in Figure 4.15 in the form of CDP plots averaged over the entire study (ca. 31 months). As discussed in previous studies, the early morning minimum reflects the loss of PAN and PPN due to the fast reactions of the RCO_3 radicals ($R = CH_3$ for PAN, $R = C_2H_5$ for PPN) with NO emitted by vehicles during the morning rush hours. The early afternoon maximum often coincides with that for ozone, consistent with the common origin (photochemical formation) of ozone and peroxyacyl nitrates. Figure 4.15 shows an average four-fold amplitude in diurnal variations, e.g., from ca. 0.4 ppb to ca. 1.6 ppb for PAN, an average interval of ca. 8 hours from the early morning minimum to the early afternoon maximum, and an average interval of ca. 16 hours from the early afternoon maximum to the early morning minimum; this interval includes a period of ca. 5 hours during which average PAN and PPN concentrations are nearly constant at night. Figure 4.16 shows CDP plots of PAN constructed from data for 2001, 2002 and 2003. These plots are essentially identical to that shown in Figure 4.15 for PAN averaged over the entire study. The CDP plots shown in Figure 4.16 are shown again in Figure 4.17 (2001), Figure 4.18 (2002) and Figure 4.19 (2003), this time with the standard deviations associated with each of the averages calculated from concentrations measured every 15 minutes. These standard deviations are a measure of the day-to-day variability in ambient concentrations. Figures 4.17, 4.18 and 4.19 indicate that the amplitude of the standard deviations was similar from one year to the next. Data for PPN, not shown, lead to identical conclusions.

On average, diurnal variations of PCE were different from those of PAN and PPN. The study-averaged CDP plot shown in Figure 4.20 is somewhat ragged (on account of the high PCE events discussed earlier) and exhibits an early morning maximum flanked by two "shoulders" of intermediate values (ca. 2 – 6 a.m. and 11 a.m. – 4 p.m.) that are separated from each other by a near-plateau of low concentrations between ca. 4 p.m. and 2 a.m. The CDP plots for 2001, 2002 and 2003 are shown together in Figure 4.21, which clearly shows the decrease in concentrations from 2001 to 2003 and also indicates, albeit less clearly, that diurnal variations in the study-averaged CDP plot shown in Figure 4.20 are dominated by those associated with the higher concentrations measured in 2001. The CDP plot for 2003 is repeated in Figure 4.22 to show that diurnal variations for that year were similar to those recorded in 2001, but with overall lower average concentrations. The CDP plot of PCE for 2003 is repeated again in Figure 4.23, this time with the standard deviations associated with each average. Figure 4.23 shows that the highest standard deviations were associated with the times at which high PCE events were recorded.

The study-averaged CDP plot shown in Figure 4.24 is for diurnal variations of the PCE/PAN concentration ratio. This plot combines the features of those shown for PAN in Figure 4.15 and for PCE in Figure 4.20. On average the diurnal variation of the PCE/PAN (or PCE/PPN, not shown) concentration ratio included a decrease from early morning (ca. 7 a.m.) to early afternoon (ca. 2 p.m.) followed by an increase from early afternoon to early morning. The average amplitude of the diurnal variations of the PCE/PAN concentration ratio was about threefold, from ca. 0.16 to ca. 0.48.

4.5 Comparison of PCE concentrations to those measured by ARB

The ambient concentrations of PCE presented and discussed in this report are from measurements made every 15 minutes. As part of the Air Toxics program, ARB measures PCE in 24-hour samples collected every 12 days. The two sets of measurements are made at the same location, i.e., the SCAQMD Azusa air quality monitoring station. As discussed earlier in this section, our measurements show that ambient PCE is highly variable from one measurement to the next. Thus, it is of interest to compare our results to those obtained by ARB in 24-hour samples. To do so, we have compiled from the ARB web site PCE concentrations measured in the 67 samples collected in Azusa between March 8, 2001 and September 18, 2003, and we have calculated the 24-hour averaged PCE concentrations from the 15-minute measurements we made on the days the ARB samples were collected.

The results of the comparison are listed in Table 4.2 and are shown in Figure 4.25. Table 4.2 includes the 24-hour PCE concentrations measured by ARB, the corresponding 24-hour averages calculated from our measurements made every 15 minutes, the corresponding PCE concentration ratios (DGA/ARB), the corresponding differences (DGA minus ARB) and the percent relative standard deviations (RSD) of these differences. Table 4.2 also includes the averages, standard deviations, and highest and lowest values of PCE concentrations, concentration ratios, concentration differences and percent RSD. The results in Table 4.2 indicate reasonable agreement between the two sets of measurements. The average PCE concentration ratio (DGA/ARB) was ca. 1.23 ± 0.35 and the average concentration difference was 30 ± 32 ppt with an average RSD of 14.5 ± 10.9 percent. Examination of the individual data in Table 4.2 indicates a higher incidence of outliers in 2001 (including the highest outlier on March 20, 2001, i.e., PCE = 320 ppt from the ARB sample and PCE = 460 ppt from the 24-hour average of our 15 minute data), perhaps reflecting the higher frequency of events of high PCE concentrations and the higher PCE concentrations recorded during high PCE events in 2001. A scatterplot of our PCE data vs. those of ARB is shown in Figure 4.25. Also included in Figure 4.25 is the least squares linear regression line, which had a slope of 1.025 ± 0.032 (Y = DGA, X = ARB) and an intercept of 26 ± 6 ppt. The two sets of measurements were highly correlated, with R^2=0.940 (n = 67, no outliers deleted).

5. SHORT-TERM VARIATIONS

Average seasonal and diurnal variations in ambient concentrations of PAN, PPN and PCE are important features of the database and have been described in section 4. It is also important to examine short-term variability features, i.e., changes that occur from one day to the next, over a few days, and over shorter periods on a given day. Concentrations of PAN, PPN and PCE vary over short periods of time due to, among others, variations in emissions (direct emissions for PCE; emissions of VOC and NO_X for PAN and PPN) and variations in meteorology (wind speed, wind direction, inversion height, rain, fog, high winds, etc.).

This section deals with short-term variations in ambient concentrations of PAN, PPN and PCE. We attempt to illustrate some of the short-term patterns (some frequent, others not) contained in the overall database. A more systematic study of the role of emissions, meteorology and other factors on short-term changes in ambient concentrations will be carried out in future work. Short-term variations of the PPN/PAN concentration ratio are discussed in section 6.

5.1 Weekdays vs. weekends

Much attention has been devoted recently to the fact that ambient concentrations of ozone in urban air are often higher on weekends than on weekdays. The factors that may contribute to this observation have been analyzed in detail and need not be repeated here (e.g., Croes, et al, 2003; also nearly all articles published in the July 2003 issue of the Journal of the Air and Waste Management Association). For PAN and PPN, which like ozone are secondary pollutants, day of the week differences in ambient concentrations may reflect day of the week differences in the magnitude and timing of emissions of precursors, i.e., VOC and NO_X. For PCE, day of the week differences in ambient concentrations may reflect activity patterns, i.e., day of the week differences in direct emissions.

We find that PAN and PPN, like ozone, are higher on weekends, while PCE is lower on weekends. These observations may be illustrated in several ways, some of which are given below as examples.

Figure 5.1 includes, for each day of the week, composite diurnal profiles of ambient concentrations vs. time of day for PAN in 2002. The data used to construct the CDP shown in Figure 5.1 are those for the entire calendar year, not just the "smog season". Similar plots, not shown, describe day of the week variations of PAN in 2001 and in 2003 and of PPN for 2001, 2002 and 2003. These CDP plots were constructed without "fine-tuning". We ignored holidays that fall on weekdays (e.g., Monday for Labor Day, Memorial Day, etc., Thursday for Thanksgiving) even though activities on holidays and on days that precede and/or follow major holidays are obviously different (vehicle traffic, industrial emissions, etc.). We also ignored the fact that many people work on a four-day schedule, e.g., Monday – Thursday or Tuesday – Friday.

While our analysis could readily be refined to better match actual activity patterns, the data in Figure 5.1 clearly show that ambient PAN is highest on Sunday, and that ambient PAN is also higher on Saturdays than on weekdays. These day of the week differences are more apparent during the daytime period of higher PAN concentrations, see the CDP plot shown in Figure 5.2 for PAN in 2002 during daytime hours (ca. 9 a.m. to 5 p.m.).

Figure 5.2 also shows day of the week differences in the time at which the maximum PAN concentration is recorded. On average, the maximum PAN concentration is observed at about the same time on Saturdays, Sundays and Mondays. A broader maximum is observed on Tuesdays, Wednesdays, and Thursdays, and the Thursday maximum occurs later in the afternoon. A different pattern is observed on Fridays with two maxima, one earlier than on any other day (ca. 12:30 PST) and the other later in the afternoon.

Figure 5.3 includes, for each day of the week, CDP plots of ambient PCE measured in 2002 (similar plots, not shown, were obtained using data for 2001 and 2003). The CDP plots for PCE include data from high PCE events (in Table 4.1 and discussion in section 4) and therefore are more ragged than those discussed above for PAN (and PPN). Nevertheless, Figure 5.3 shows that on average ambient concentrations of PCE decreased on Saturday evening and remained low until early morning (ca. 7 a.m.) on Monday.

Table 5.1 summarizes some of the features shown in Figure 5.1, Figure 5.2 and Figure 5.3. Table 5.1 includes, for each day of the week, the 2002-averaged PAN and PCE concentrations and their ratios to those measured on Sunday. Sunday/other day ratios ranged from 1.04 (Saturday) to 1.25 (Tuesday) for PAN and from 0.54 (Thursday) to 0.76 (Monday) for PCE. As noted above, results for PPN in 2002 were similar to those for PAN, and results for 2001 and 2003 were similar to those for 2002, i.e., PAN and PPN were higher on Sundays than on weekdays and the reverse was observed for PCE.

5.2 Screening of the database for short-term variations

As an aid to identify periods of interest with respect to short-term variations in ambient concentrations of PAN, PPN and PCE, we used times series plots of monthly averages and composite diurnal profile plots of monthly averaged concentrations vs. time of day. Examples of these plots can be found in section 4. From the data used to construct these plots, we extracted the minimum and maximum PAN, PPN and PCE concentrations, and constructed time series and CDP plots of concentration minima and concentration maxima. Examples of these plots are shown in Figure 5.4, Figure 5.5 and Figure 5.6. Figure 5.4 shows a time series plot of PAN minima for the entire study. CDP plots of PAN and PCE minima for 2001, 2002 and 2003 are shown in Figure 5.5 and Figure 5.6, respectively. These plots, together with the time series plots of all individual data shown in section 3, proved useful to shorten the time-consuming task of screening the entire database for examples of short-term variations, both typical and unusual. The database for PPN/PAN ratios was screened in a similar manner. Short-term variations of the PPN/PAN ratio are discussed in section 6.

5.3 High PCE events

As noted earlier, short-term variations in ambient PCE were more frequent and of larger amplitude than those of PAN and PPN. The compilation of high PCE events given in Table 4.1 also indicates that the frequency and magnitude of these events decreased from 2001 to 2003. High PCE events involved single or multiple observations of high PCE concentrations. For example, a single observation of high PCE, ca. 11 ppb, was made in the morning of November 29, 2001. As is shown in Figure 5.7, all other ambient PCE concentrations on that day were less than ca. 1 ppb. Figures 5.8, 5.9 and 5.10 show examples of multiple observations of high PCE concentrations. Those shown in Figure 5.8 were recorded in a narrow period near midnight on

March 30 – 31, 2001; those shown in Figure 5.9 were recorded in the morning of October 26, 2001, and those shown in Figure 5.10 were recorded throughout the daytime hours on April 9, 2001.

5.4 High PAN and PPN concentrations outside of the smog season

As noted before in the few long-term studies of PAN carried out prior to this work (Grosjean, 2003), episodes of high concentrations of PAN are not confined to the traditional smog season. For example, Figure 5.11 shows a two-day episode on March 30 – 31, 2001 with elevated PAN and PPN concentrations (high levels of PCE were also recorded near midnight, see Figure 5.8). On both days several maxima were observed, three on March 30 and two on March 31. As another example, Figure 5.12 shows high PAN and PPN concentrations on November 13, 2002, with again three maxima recorded in the afternoon hours.

5.5 Variations of the time of maximum PAN and PPN concentrations

As discussed in section 4, average diurnal variations of PAN and PPN included a maximum in the afternoon. While this feature was indeed recorded on many days, there was significant variability in the number of maxima recorded on a given day and in the time of day at which these maxima were recorded. First, shifts in wind direction often resulted in observations of several maxima in the afternoon, as was the case on the days shown above in Figure 5.11 and Figure 5.12. Even on the more frequent days when only one afternoon maximum was recorded, changes in wind speed and direction resulted in day-to-day changes of the time at which the maximum was observed. This variability is illustrated in Figure 5.13, which includes CDP plots of maximum PAN for 2001, 2002 and 2003. Maximum PAN concentrations, while broadly centered in the early afternoon, could occur at any time between early and late afternoon on any given day, e.g., the maximum PAN concentration of ca 5.4 ppb was recorded at 3:45 p.m. on May 28, 2003.

On less frequent occasions, high PAN (and PPN) concentrations were recorded in the early morning (e.g., ca. 2.7 ppb at 9:00 a.m. on September 2, 2002), in the late evening (e.g., ca. 2.7 ppb at 10:00 p.m. on September 20, 2003) or at night (e.g., ca. 2.6 ppb at 2:30 a.m. on August 24, 2001, ca. 2 ppb at 3:30 and 3:45 a.m. on September 11, 2003, and up to ca. 3 ppb at 5:00 to 5:30 a.m. on August 15, 2003). The nighttime peaks in PAN concentrations observed during this study have also been observed in earlier work (Grosjean, 2003). They have been attributed to nighttime, downslope winds bringing polluted air masses (including ozone and PAN) from the preceding day over the monitoring location. These peaks are suppressed at the onset of the morning vehicle commute since vehicle-emitted NO is a sink for both ozone and peroxyacyl nitrates.

5.6 Other short-term variations

Depending on the interplay between emissions and meteorology, short-term variations may be recorded that affect PAN (and PPN), PCE, or both. The seven figures shown here are presented to illustrate the diversity of short-term variations that were observed during this 31-month study. These and other episodes of interest will be analyzed in more detail in future work.

On several instances the concentration of PCE was "flat" (little or no variations) for periods ranging from several hours to several days. This was the case between 10 a.m. and 7 p.m. on November 27, 2001 (Figure 5.14), between 8 a.m. and 2 p.m. on December 29, 2001, during which it rained in Azusa (Figure 5.15), all night on December 25 – 26, 2001 (Figure 5.16) and for a period of ca. 48 hours on November 25 – 28, 2002 (Figure 5.17). The time series plots shown in Figures 5.14 to 5.17 indicate that concentrations of PCE were low during these periods of "flat" PCE concentrations. For the four episodes shown in Figures 5.14 to 5.17, concentrations of PAN and PPN were also nearly "flat" throughout the periods of "flat" PCE concentrations. This was not the case, however, during other periods of "flat" PCE concentrations. For example, PCE was low and nearly constant during the night of December 22 – 23, 2002, but concentrations of PAN exhibited substantial variations during the same period (Figure 5.18). Similarly PCE remained low and nearly constant for ca. 25 hours on January 5 – 7, 2003 but during that period PAN first increased steadily for ca. 20 hours and then decreased for ca. 5 hours (Figure 5.19). The last figure in this section (Figure 5.20) shows concentrations of PAN, PPN and PCE on October 15 – 17, 2002, during which fog was present. During that period PAN was high throughout the night, decreased in the morning, decreased again in the afternoon of October 16, increased again, and remained nearly constant throughout the following night.

6. PPN/PAN CONCENTRATION RATIO

6.1 General considerations

Previous studies of ambient PPN in southern California have been of short duration, and most of these studies have been carried out in summer (Grosjean, 2003). The present study offers, for the first time, an opportunity to examine in detail the long-term, seasonal, short-term and diurnal variations of the PPN/PAN concentration ratio.

PAN and PPN are formed in the atmosphere in a similar manner. They are also removed from the atmosphere in a similar manner. Both PAN and PPN form in-situ (they have no known direct sources) in photochemical reactions involving VOC (hydrocarbons, carbonyls) and oxides of nitrogen. PAN forms from VOC that produce acetyl radicals (CH_3CO). PPN forms from VOC that produce propionyl radicals (CH_3CH_2CO). Thus, some VOC are precursors to PAN, other VOC are precursors to PPN, and some VOC are precursors to both. Both PAN and PPN are removed predominantly by thermal decomposition (removal by photolysis is negligible at ground level; removal by reaction with OH is negligibly slow for PAN and is ca. 10 times faster for PPN but is still negligible in first approximation for the typical air mass transport times to Azusa). Thermal decomposition is of comparable magnitude for PAN and PPN, increases rapidly with increasing temperature, and, at a given temperature, increases with increasing NO/NO_2 concentration ratios.

We have described in section 4 and section 5 how ambient concentrations of PAN and PPN in Azusa varied substantially with time and have discussed the corresponding diurnal, day-to-day and seasonal variations. Air masses sampled in Azusa contain PAN and PPN at concentrations that result, at any given time, from the extent of their formation offset by the extent of their removal. Since PAN and PPN have similar formation (photochemical production) and loss (thermal decomposition) process, one would expect, in general, a close association between ambient concentrations of PAN and PPN measured at the same time. Indeed, the results of this study show that, on average, the PPN/PAN concentration ratio was nearly constant. The results also show average seasonal and average diurnal variations as well as short-term variations. These variations in the ambient PPN/PAN concentration ratio may result from variations in formation rates, e.g., variations in the abundance of VOC that are precursors to PAN relative to that of VOC that are precursors to PPN, from variations in the relative magnitude of loss processes, or both.

6.2 Overview of results

As mentioned in section 3, ambient PAN and ambient PPN measured in Azusa between February 2001 and September 2003 both exhibited lognormal distributions. Plots of log PPN vs. log PAN are shown in Figure 6.1 for 2001, Figure 6.2 for 2002, and Figure 6.3 for 2003. The three plots indicate, on average, a high degree of correlation between log PPN and log PAN. The three plots also indicate the occurrence of higher (than average) and lower PPN/PAN ambient concentration ratios. Scatterplots of PPN vs. PAN, not shown, also indicated a high degree of correlation between PPN concentrations and PAN concentrations. Linear least squares regressions of PPN vs. PAN yielded slopes, intercepts and correlations coefficients of 0.119 ± 0.0001, $-0.006 \pm$

0.0001 ppt, $R^2 = 0.984$ for 2001, 0.124 ± 0.0001, -0.005 ± 0.0001 ppt, $R^2 = 0.983$ for 2002, and 0.122 ± 0.0001, -0.005 ± 0.0001 ppt, $R^2 = 0.986$ for 2003.

Histograms of the PPN/PAN concentration ratios are shown in Figure 6.4 (2001 data), Figure 6.5 (2002 data) and Figure 6.6 (2003 data, also shown earlier in section 3). The three plots are similar and show that PPN/PAN ratios were normally distributed.

The close association between ambient PPN and ambient PAN is also illustrated by the scatter plot of monthly averages shown in Figure 6.7. Monthly averages were highly correlated (R^2 = 0.983) with a linear regression slope of 0.115 (PPN vs. PAN) and a near-zero intercept (0.2 ppt). Figure 6.8 shows no correlation between the PPN/PAN ratio of monthly averaged concentrations and the corresponding monthly-averaged PAN concentrations ($R^2 = 0.058$).

6.3 Average seasonal variations

Average seasonal variations of the PPN/PAN ratio are described using monthly data. Using all data for a given month, we carried out least squares linear regressions of PPN concentrations vs. PAN concentrations, and vice versa. We then examined the seasonal variations of the corresponding slopes and other regression parameters. We also constructed monthly-averaged composite diurnal profiles (CDP) and examined the shape of these CDP for possible seasonal variations.

Listed in Table 6.1 are the parameters obtained by least squares linear regression, for each month, of all PPN concentrations vs. PAN concentrations, and vice versa. The parameters listed in Table 6.1 include the slope and its standard deviation, the intercept and its standard deviation, the correlation coefficient, and the percent ratio of the intercept to the average concentration (average concentrations are given in Table 3.1). Also included in Table 6.1 are regression parameters for each calendar year and for the entire study. The data in Table 6.1 indicate close association between PPN and PAN throughout the study (high R^2). Regression slopes varied little from one month to the next, e.g., for the PPN/PAN ratio these slopes ranged from 0.108 to 0.131 and averaged 0.119 for 2001, 0.124 for 2002, 0.122 for 2003, and 0.122 for the entire study.

Within this narrow range of concentration ratios, seasonal variations are suggested by the time series plots of the monthly slopes and monthly intercepts shown in Figure 6.9 and Figure 6.10, respectively, for the PAN/PPN ratio. Figure 6.9 indicates a tendency for the PAN/PPN slopes to be higher during the winter months. Figure 6.10 indicates a tendency for the PAN/PPN intercepts to be higher during summer.

The possible seasonal trend for the slopes, which is not as distinct as that for intercept, needs to be examined in more detail. The seasonal trend for intercepts may be associated with formation of PAN, during summer, by VOC that do not produce PPN. There are several possible scenarios consistent with this hypothesis. One scenario involves biogenic hydrocarbons, e.g., isoprene and terpenes such as alpha-pinene produce PAN but not PPN, and emissions of biogenic hydrocarbons increase during summer (there are, however, biogenic hydrocarbons, such as cis-3-hexen-ol, that produce PPN). Another scenario involves seasonal changes in the relative abundance of VOC emitted by vehicles and that are precursors to PAN and PPN. Such seasonal shift may result from changes in gasoline composition (e.g., summer grade), in the relative abundance of evaporative vs. exhaust emissions, and, for exhaust emission, in the relative abundance of hot-stabilized vs. off-cycle emissions. Further analysis of the role of VOC with regard to average seasonal changes in the PPN/PAN ratio would be of interest. However, we stress again that average seasonal changes in the PPN/PAN ratio were small, and that these small changes may be due to seasonal differences in loss rates rather than from (or in addition to) changes in rates of production.

6.4 Average diurnal variations

To examine average diurnal variation of the PPN/PAN ratio, we have constructed CDP plots of PPN/PAN vs. time of day for the entire study, for each year, and for each month. All plots exhibit the same feature. They show that, within the small range of time-averaged ratios measured throughout the study, the PPN/PAN ratio exhibits well-defined diurnal variations with two maxima, one at night and the other in the afternoon. Figure 6.11, 6.12, 6.13 and 6.14 show CDP plots of the PPN/PAN ratio for the entire study and for the years 2001, 2002 and 2003, respectively. Standard deviations are included. They indicate more variability in the data at night than during the day. The CDP plots for 2001, 2002 and 2003 are repeated together in Figure 6.15 with the standard deviations omitted to facilitate comparison. The diurnal profiles shown in Figure 6.15 are similar for all three years, but PPN/PAN ratios measured in 2001 were on average lower throughout the day than those measured in 2002 and 2003. The nighttime maximum was higher in 2003 than in 2002, and the reverse was observed for the afternoon maximum.

CDP plots of monthly-averaged data are shown in Figures 6.16 for 2001, Figure 6.17 for 2002, and Figure 6.18 for 2003. Most of the monthly-averaged data exhibited the same diurnal features as those discussed above for yearly-averaged and study averaged CDP plots, i.e., they exhibited two maxima, one at night and the other in the afternoon. The time of the two maxima varied little from one month to the next. Similarly the time of the two minima (one in the early morning and the other in the late afternoon, coinciding with the NO_X peaks from morning and evening vehicle traffic) varied little from one month to the next. The relative magnitude of the nighttime maximum and the afternoon maximum appears to vary with season. Nighttime maxima were generally higher than afternoon maxima in winter. The reverse was often observed during late spring and summer. For example, afternoon maxima were higher than those recorded at night in August and September 2001 (Figure 6.19), June and July 2002 (Figure 6.20) and June 2003 (Figure 6.21). The CDP for June 2003 is repeated in Figure 6.22, this time with the corresponding standard deviations. Higher daytime maxima have also been recorded in previous studies, all carried out during summer, of PAN and PPN at several southern California locations in 1989, 1990, 1991, 1993 and 1997 (Grosjean, 2003).

Having shown that, on average, the PPN/PAN ratio includes two maxima, one at night and the other in the afternoon, it is of interest to examine further the diurnal variations of the PPN/PAN ratio as they relate to the diurnal variations of PAN and of PPN. Using data for 2003 as an example, Figure 6.23 shows that on average the afternoon maximum of the PPN/PAN ratio does not coincide with the afternoon maximum in PPN and PAN concentrations but occurs somewhat later. Further examination of the data in Figure 6.23 (data for 2001 and 2002 lead to the same observations) show that the average diurnal variations of the PPN/PAN ratio may be divided into three phases. These three phases are defined by the two minima and the nighttime maximum in PPN/PAN ratios. The first phase corresponds to the morning and afternoon hours between the morning and evening minima of the PPN/PAN ratio. During this phase the PPN/PAN ratio varies in the same way as the PAN and PPN concentrations, i.e., the ratio first increases with increasing PAN and PPN and then, after a lag as noted above, decreases with decreasing PAN and PPN. In the other two phases, the PPN/PAN ratio varies in the opposite direction of the PAN and PPN concentrations. The second phase corresponds to the late evening and night period defined by the evening minimum and nighttime maximum of the PPN/PAN ratio. During this phase the PPN/PAN ratio increases while PAN and PPN concentrations decrease. The reverse is observed during the third phase, i.e., the PPN/PAN ratio decreases while PAN and PPN concentration increase between the nighttime maximum and the morning minimum in PPN/PAN concentration ratios.

The three phases in the average diurnal variation of the PPN/PAN ratio are illustrated in Figure 6.24, in which we plotted the average PPN/PAN ratio for 2003 vs. the corresponding PPN concentrations. The points in Figure 6.24 are the 2003-averaged values of PPN concentrations and PPN/PAN concentration ratios measured every 15 minutes. Thus presented, the data appears as two large loops connected by a smaller loop. The large loop on the right side of the plot is that defined above as the first phase, during which PPN/PAN ratios vary in the same direction as PPN and PAN concentrations, i.e., the ratios increase when PAN and PPN increase from morning to afternoon and then decrease when PAN and PPN decrease from afternoon to evening. The second large loop, located on the left side of the plot, corresponds to the other two phases during which PPN/PAN ratios vary in the opposite direction of PPN and PAN concentrations.

6.5 Weekdays vs. weekends

We have shown in section 5 that ambient concentrations of PAN and those of PPN are on average higher on weekends than on weekdays. We examine here whether the PPN/PAN concentration ratio also shows differences between weekdays and weekends. To do so, we have constructed composite diurnal profiles of the PPN/PAN ratio for each day of the week. An example is given in Figure 6.25, which show day of the week-averaged CDP for all 2002 data. Figure 6.25 shows the same features as those discussed in the preceding section for the overall data, i.e., on average the PPN/PAN ratio exhibits diurnal variations with two maxima (night and afternoon) and two minima (morning and evening). Data for 2001 and for 2003, not shown, exhibit the same features as those shown in Figure 6.25 for the 2002 data. Overall, the data do not show higher PPN/PAN concentration ratios on weekends as compared to weekdays. There are, however, day of the week differences in the relative magnitude of the nighttime and afternoon maxima, with the caveat that we did not "fine tune" the database (by, for example, including holidays that fall on weekdays) and that the plots shown in Figure 6.25 are for the entire year, not just the smog season. For example, the afternoon peak in PPN/PAN ratios is higher than the nighttime peak on Monday, the reverse is observed on Tuesday, Thursday, Friday and Saturday, and the two peaks are of comparable magnitude on Wednesday and Sunday. The nighttime maximum is on average highest on Thursday and Saturday and lowest on Monday and Tuesday, and the afternoon is on average lowest on Friday and highest on Wednesday, Thursday, Saturday and Sunday. These day of the week differences in the average diurnal variations of the PPN/PAN concentration ratio may reflect day of the week differences in meteorology, in the magnitude and timing of NO_X and VOC emissions, and/or in the composition of VOC that are precursors to PAN and PPN. Further analysis of the data is limited by the lack of data for speciated VOC, which are only measured during summer and with limited time resolution as part of PAMS.

6.6 Short-term variations

We have described in the previous sections the average seasonal and average diurnal variations of the PPN/PAN concentration ratio, and have shown that on average the ratio exhibited well-defined temporal variations. We have also shown in section 5 that short-term variations in ambient concentrations of PAN and PPN did not necessarily follow the patterns expected from analysis of average data. This was also true for the PPN/PAN ratio, whose short-term variations reflected the substantial short-term variations discussed earlier for ambient concentrations of PAN and PPN.

To illustrate short-term variations of the PPN/PAN concentration ratio, we present below two groups of plots. The first group consists of CDP plots of the PPN/PAN maxima and minima. The second group includes specific examples of high or low PPN/PAN ratios recorded during the study.

CDP plots of the PPN/PAN maxima are shown in Figure 6.26, Figure 6.27 and Figure 6.28 for 2001, 2002 and 2003, respectively. The three figures show that PPN/PAN ratios were on occasion as high as ca. 0.3 – 0.4. These figures also show that episodes of high PPN/PAN ratios were often recorded in the late evening and at night.

CDP plots of the PPN/PAN minima are shown in Figure 6.29, Figure 6.30 and Figure 6.31 for 2001, 2002 and 2003, respectively. The three figures show that on occasion the PPN/PAN ratios were as low as 0.03 – 0.04. The figures also show that episodes of low PPN/PAN ratios were often recorded in the late evening and at night. Overall, the results shown in Figures 6.26 to 6.31 indicate that episodes of low PPN/PAN ratios and episodes of high PPN/PAN ratios were both often recorded in the late evening and at night, and that the PPN/PAN ratio was as much as ca. 10 times higher during high ratio episodes than during low ratio episodes.

Figure 6.32 shows an example of episode during which the PPN/PAN ratio was high. On December 28 – 29, 2001, PAN exhibited its "usual" variations with a mid-afternoon maximum, decreased steadily in the evening and at night, and increased again on the following day with two maxima, one in the afternoon and the other in the late evening. The PPN/PAN ratio was ca. constant throughout the first day's morning and afternoon (at a "typical" value of ca. 0.12) and then increased steadily as PAN decreased in the evening and at night. The PPN/PAN ratio reached a high value of ca. 0.42 at night and decreased again to ca. 0.10 – 0.12 on the following day. During this period, PPN decreased in the evening until ca. 7 p.m., remained nearly constant until 2 a.m., and then decreased again along with PAN.

Figure 6.33 shows an example of episode during which the PPN/PAN ratio was low. On August 28 – 31, 2001, PAN and PPN exhibited typical summer diurnal variations with afternoon maxima and minima at night. The PPN/PAN ratio decreased sharply at night on August 28 and again on August 31, with minima of ca. 0.03 on both nights. In the time interval between these two minima, the PPN/PAN ratio returned to diurnal variations that are typical for summer (see discussion in section 6.4) and ranged from ca. 0.08 at night to ca. 0.12 in the afternoon.

7. LONG-TERM TRENDS

7.1 Scope and contents of this section

We examine in this section the long-term trends in ambient levels of PAN and PPN in southern California, where PAN and PPN were first measured in 1960 and 1962, respectively. Examination of long-term trends is of value to place recent results in perspective and to assess the effectiveness of regulatory measures (e.g., emission controls, changes in vehicle fuel composition) aimed at improving urban air quality.

The long-term trends in ambient PAN and PPN from 1960 to 1997 have been discussed in detail by Grosjean (2003; see Appendix B in this report), who compiled data for ca. 35 studies, examined peak concentrations, 24 hour averages and monthly averages, discussed gaps in the data record, and stressed that long-term trends constructed from disparate data sets must be viewed with caution. In this section, our objective is simply to include the results of the present study in the data record and to examine how results obtained after 1997 fit into the overall historical record of ambient PAN and PPN in southern California. We first examine long-term trends for PAN, for which much more information is available than for PPN. We also examine the more limited data for PPN and for the PPN/PAN concentration ratio.

7.2 Long-term trends for ambient PAN

Long-term trends for ambient PAN are illustrated in the time series plots of peak concentrations, highest 24 hour-averaged concentrations and highest monthly averaged concentrations shown in Figure 7.1, Figure 7.2 and Figure 7.3, respectively. The information used to construct Figure 7.1

consists of the data shown in Figure 1 of Grosjean (2003) augmented by data from studies carried out since 1997. The information used to construct Figure 7.2 and Figure 7.3 consists of the data compiled in Table 2 of Grosjean (2003) augmented by data from studies carried out since 1997.

Data are not available for all years. For those few years during which PAN was measured at more than one location, typically as part of short-term studies carried out during summer, only the highest values measured during that year, irrespective of location, are shown in Figures 7.1, 7.2 and 7.3. More data are available for peak concentrations (Figure 7.1) than for 24 hour-averaged concentrations (Figure 7.2). Less data are available for monthly averaged concentrations (Figure 7.3) since few studies have been of sufficient duration to yield monthly averages.

The data in Figure 7.1, Figure 7.2 and Figure 7.3 show a substantial decline in ambient levels of PAN from the 1960's to the 1990's. The data also show no indication of a downward (or upward) trend in the last ten years. This statement should be viewed with caution since it is based on data from few studies that varied in scope (including the number of locations) and duration. During the last decade, we have measured PAN in three studies carried out in 1993 (Grosjean et al, 1996), 1997 (Grosjean et al, 2001) and 2001 – 2003 (this study). The 1993 and 1997 studies are described briefly below.

The 1993 study involved short-term measurements (ca. 2 weeks) during summer at four locations. The period studied included the most severe smog episode recorded in 1993, and the highest PAN concentrations measured during that smog episode may have been the highest PAN concentrations at these locations in 1993. The peak PAN concentrations measured during the 1993 study were 5.5 ppb in Long Beach, 6.1 ppb in Azusa, 6.9 ppb in downtown Los Angeles, and 9.9 ppb in Claremont.

The next study was carried out in summer 1997 as part of SCOS97-NARSTO. PAN was measured at two locations, Azusa and Simi Valley. The peak PAN concentrations were 4.8 ppb in Azusa and 3.0 ppb in Simi Valley. The study was of sufficient duration to yield monthly averaged concentrations at both locations (August and September in Azusa, and July, August and September in Simi Valley). The study was carried out during a period of higher-than-usual temperatures (El Nino), and calculations described in Grosjean et al (2001) show that more PAN was lost by thermal decomposition during summer 1997, and this more so in warmer Azusa than in Simi Valley. Grosjean et al (2001) concluded that, taking thermal decomposition into account, PAN concentrations measured in 1997 in Azusa would have been similar to those measured in 1993 at the same location.

Peak concentrations measured in this study were ca. 7.4 ppb in 2001, 6.4 ppb in 2002, and 6.5 ppb in 2003. They are higher than that measured in Azusa in summer 1997 (4.8 ppb) and slightly higher than that measured in Azusa in summer 1993 (6.1 ppb). The small differences between the 1993, 1997 and 2001 – 2003 studies do not indicate a distinct trend. For comparison, the only other study carried out in Azusa prior to the three studies discussed above was carried out in summer 1987 as part of SCAQS (Williams and Grosjean, 1990) and yielded a peak PAN concentration of 13 ppb, i.e., about twice as high as those measured in 1993, 1997 and 2001 –2003 (see Figure 7.4, which compares the composite diurnal profiles of PAN measured in Azusa in 1987, 1993, 1997 and in the present study). The highest 24 hour-averaged concentrations measured in 1993 and 1997 were comparable in magnitude to those measured in 2001, 2002 and 2003. Similarly, the monthly-averaged concentrations measured in 1997 (the 1993 study was of short duration) were comparable to, and slightly lower than (perhaps on account of higher temperatures in summer 1997), those measured in the present study (Table 7.1).

Overall, the data from studies carried out in the last decade (1993 – 2003) give no indication of a change in ambient PAN concentrations. This "flat" trend in recent years follows a 30 year trend of decreasing PAN concentrations. During the last decade, there have been major changes in vehicle fuel composition, including the introduction of California Phase 2 reformulated gasoline in 1996 (i.e., between our 1993 and 1997 studies) and the more recent changes resulting from the phasing out of MTBE that preceded its official ban on December 31, 2003. These and other regulatory actions have impacted the composition and reactivity of vehicle-emitted VOC. They have also resulted in changes in NO_X emissions and in the VOC/NO_X ratio. In first approximation, these and other changes have had little impact on ambient levels of PAN.

7.3 Comparison of seasonal variations

It is of interest to examine the historical data for possible changes in seasonal variations. Only three long-term studies of ambient PAN have been carried out in southern California prior to this study (Taylor, 1969, Pitts and Grosjean, 1979, Temple and Taylor, 1983). All three studies were carried out at the same location, Riverside, in August 1967 – April 1968 (9 months), May 1975 – October 1976 (18 months) and January – April and August – December 1980 (4 months and 5 months).

We compare the results of these studies to that of the present work for two parameters, the highest PAN concentration measured in a given month (Figure 7.5) and the monthly-averaged PAN concentration (Figure 7.6). The comparison indicates no major seasonal shift in ambient PAN. The comparison shows, as discussed earlier, how ambient levels of PAN have substantially decreased between 1960 – 1980 and the early 2000's. The data from the earlier studies also show that high concentrations of PAN were often recorded outside of the traditional smog season (e.g., 58 ppb in November 1967, 25 ppb in November 1975 and in January 1976, 35 ppb in April 1980). As discussed in section 5, our results also include, albeit with much lower concentrations than those measured ca. 20 – 35 years ago, episodes of elevated PAN and PPN outside of the smog season.

7.4 Long-term trends for ambient PPN

Much less data are available for ambient PPN than for ambient PAN. The compilation given in Table 3 of Grosjean (2003) includes one measurement made in 1962 in Riverside, a 12-day study made 17 years later during spring in East Los Angeles, and a 10-day study made 5 years later in Downey during winter. It is only in 1989 that PPN was measured for over two months at a mountain location (Tanbark Flat) during summer (Williams and Grosjean, 1991). Thus, no trend could be examined for the 27 year period 1962 – 1989 due to the paucity of data. We note, however, that the highest PPN concentration measured at Tanbark Flat during summer 1989, 5.1 ppb, compares to that of 6 ppb measured (along with 50 ppb of PAN) in Riverside in 1962.

Starting in 1989, PPN was measured more frequently, i.e., at 3 locations in 1989, one location in 1990, two locations in 1991, four locations in 1993 (including Azusa), two locations in 1997 (again including Azusa), and in Azusa in 2001 – 2003 (this study). The peak PPN concentrations and the highest 24 hour-averaged concentrations measured in these studies are plotted in Figure 7.7. The highest values are from the three earlier studies, which were carried out at a mountain location, Tanbark Flat. Mountain locations that border the Los Angeles basin often experience higher levels of photochemical pollution. This has been, and continues to be, well documented for ozone. Thus, our data for Tanbark Flat may not be representative of PPN and PAN air quality within the Los Angeles basin. The data for Azusa, Claremont, Long Beach, Los Angeles in 1993, Azusa and Simi Valley in 1997, and Azusa in 2001 – 2003 (this study) do not indicate a trend in ambient PPN during the last decade.

7.5 Long-term trends for the PPN/PAN concentration ratio

The paucity of data for PPN discussed above also makes it difficult to examine trends in the PPN/PAN concentration ratio between 1962 and 1989. The PPN/PAN ratio was 0.12 in 1962 (a single measurement in Riverside), 0.145 in April 1979 (East Los Angeles), and 0.05 in February 1984 (Downey). PPN/PAN ratios measured since 1989 are shown in Figure 7.8, which we constructed from data in Table 4 of Grosjean (2003) and the results of this study. For all but two studies, the data shown in Figure 7.8 are the slopes of the least squares linear regressions (Y = PPN, X = PAN) of all concentrations measured during a given study. The slopes are shown in Figure 7.8 with their standard deviations. For the two short studies (ca. 2.5 days each) carried out in summer 1989 in Perris and Palm Springs, regression analysis was not reported and Figure 7.8 includes the range of PPN/PAN concentration ratio at the time the maximum PPN concentration was recorded.

Figure 7.8 shows study-to-study variations in the PPN/PAN ratio, with again the three highest regressions slopes being measured at Tanbark Flat (the 1989 value was 0.28; those measured in 1990 and 1991 were lower, 0.18 and 0.19, respectively). For studies carried out in the Los Angeles basin, all slopes fall within a narrow range of ca. 0.10 – 0.17. Within that small range, the lowest values were measured in Claremont in 1993 (0.10) and in Azusa during this study (ca. 0.12). In Azusa, the slopes were 0.166 in summer 1993, 0.174 in summer 1997, and, in this study, 0.119 in 2001, 0.124 in 2002, and 0.122 in 2003. Thus, the range of slopes measured in Azusa during the last decade is narrower than that for slopes measured at four locations during the same ca. 12 day period in summer 1993.

We also note that the lowest PPN/PAN ratio (0.06 Downey, winter 1984) and the highest PPN vs. PAN regression slope (0.28 in Tanbark Flat, summer 1989) are within the range of variations of the PPN/PAN ratios of ca. 0.03 to ca. 0.42 observed in this study (see section 5). Overall, consistent with data for PAN concentrations and data for PPN concentrations, data for the PPN/PAN concentration ratio show no trend in southern California over the last decade.

8. COMPARISON OF AMBIENT PAN, PPN AND OZONE

8.1 Scope and contents of this section

Peroxyacyl nitrates and ozone do not have direct sources and are formed in the atmosphere by photochemical reactions. Ozone forms in reactions involving NO_X and virtually all reactive VOC. Peroxyacyl nitrates form in reactions involving NO_X and those reactive VOC that yield peroxyacyl radicals (CH_3CO_3 for PAN, $C_2H_5CO_3$ for PPN, and so on). Ozone is removed from the atmosphere by reaction with NO and by reactions with unsaturated VOC (e.g., alkenes, terpenes, unsaturated oxygenates). Peroxyacyl nitrates are removed by thermal decomposition, with the rate of removal increasing with increasing temperature and with increasing NO/NO_2 concentration ratio. It is of interest to examine how similarities and differences in formation and removal processes affect diurnal, seasonal and other variations of ambient PAN and PPN as compared to those of ambient ozone.

In this section, we briefly describe ambient ozone measured in Azusa during the period PAN and PPN were measured, i.e., from February 2001 to September 2003. The ozone data used in this section consist of one-hour concentrations available from the California Air Resources Board. We compare seasonal and diurnal variations of ambient ozone to those of ambient PAN and PPN, and examine variations of the daily maximum ozone and PAN concentrations and of the ratio of these maxima. We also compare long-term trends in ambient ozone to those discussed in section 7 for PAN and PPN. For economy of presentation, the figures in this section show data for one peroxyacyl nitrate (e.g., PAN) and one year (e.g., 2002). Results for other years, for the entire study and for PPN vs. ozone were entirely consistent with those shown in the figures selected to illustrate the findings described in this section.

8.2 Ambient ozone in Azusa, 2001 – 2003

All one-hour ozone concentrations measured in Azusa in 2002 are shown as a time series plot in Figure 8.1. The time series plot indicates that, while ozone is 40 ppb or less most of the time, there are frequent occurrences of higher one-hour concentrations, e.g., up to ca. 140 ppb in 2002. These higher concentrations are more frequently recorded between late spring and early fall ("smog season"). This seasonal feature in variations of ambient ozone is more apparent in Figure 8.2, in which only the daily maximum one-hour ozone concentrations have been plotted to improve clarity. The three-year time series plot shown in Figure 8.2 indicates that daily maxima increase in magnitude from winter to summer, reaching values of ca. 190 ppb in 2001, ca. 140 ppb in 2002, and ca. 150 ppb in 2003.

In addition to strong seasonal variations (summer > winter), ambient ozone exhibited well-defined diurnal variations with early morning minima and early afternoon maxima. These diurnal variations, which have been documented numerous times in the air quality literature, are illustrated by the plot, shown in Figure 8.3, of all 2002 ozone data vs. time of day (no data are shown for 4 a.m., the time at which automated daily instrument zero and span are carried out). Figure 8.3 shows that in general the highest ozone concentrations are recorded in the early afternoon (ca. 2 p.m.), consistent with the geographical location of Azusa within the Los Angeles area and with prevailing meteorology.

8.3 Average diurnal variations of PAN and ozone

From the data shown in Figure 8.3, we have constructed the composite diurnal profile (CDP) of ozone in Azusa in 2002. The CDP is shown in Figure 8.4, which also includes for comparison the CDP for PAN presented earlier in this report. Figure 8.4 shows that on average diurnal variations of PAN (and PPN) follow closely those of ozone. This similarity in average diurnal variations has been noted many times, in Southern California and elsewhere.

8.4 Concentrations of PAN vs. those of ozone measured at the same time

While on average variations of PAN followed closely those of ozone with respect to time of day, see Figure 8.4 above, concentrations of PAN showed little or no correlation with those of ozone measured at the same time. Figure 8.5 shows a scatterplot of all 2002 PAN concentrations vs. the corresponding ozone concentrations. We examined several types of equations that may fit the data, e.g., polynomial, exponential (shown in Figure 8.5, with poor fit, i.e. $R^2 = 0.25$) and log-log. A log-log plot of the 2001 data is shown in Figure 8.6, along with the polynomial equation that yielded mediocre fit to the data, i.e., $R^2 = 0.645$.

8.5 Comparison of daily ozone maxima and daily PAN maxima

A time series plot of daily ozone maxima and daily PAN maxima for 2001 is shown in Figure 8.7. For both ozone and PAN, daily maxima tend to increase from winter to summer. This seasonal trend is more apparent when plotting the same 2001 data in logarithmic form, as is shown in Figure 8.8. Both Figure 8.7 and Figure 8.8 indicate poor association between daily

PAN maxima and daily ozone maxima, as does Figure 8.9, which shows substantial scatter (R^2 = 0.72) when plotting daily PAN maxima vs. the corresponding daily ozone maxima.

8.6 PAN/ozone concentration ratios

The results presented in sections 8.4 and 8.5 above indicate poor association between concentrations of PAN and those of ozone. We examine in this section the seasonal and diurnal variations of the PAN/ozone concentration ratio. Figure 8.10 shows a time series plot of all 2002 data. Figure 8.10 shows substantial variability in the PAN/ozone concentration ratios, with low values being recorded throughout the year and high values being recorded from mid-winter (e.g., mid-February 2001) to early fall (e.g., mid-October 2001). The variability in PAN/ozone concentration ratios is also illustrated by the examples of variations on specific days that are shown in Figure 8.11 (July 7, 2002; the day the highest concentration of PAN was recorded in 2002, i.e., 6.1 ppb along with 133 ppb of ozone), Figure 8.12 (August 30 – 31, 2002, during which the highest 2002 PAN/ozone ratio was recorded), and Figure 8.13 (March 23 – 24, 2002, during which the lowest 2002 PAN/ozone ratio was recorded).

The PAN/ozone concentration ratios showed no seasonal variations but exhibited well-defined diurnal variations. This is illustrated in Figure 8.14, in which all 2002 PAN/ozone concentration ratios are plotted vs. time of day. Figure 8.14 and the CDP of 2002 PAN/ozone ratios shown in Figure 8.15 (along with the similar CDP plot of 2002 PPN/ozone ratios) indicate that the PAN/ozone ratio decreases from early morning to mid-afternoon, increases from mid-afternoon to evening, and decreases again at night. While a more detailed examination of these diurnal variations would require NO, NO_2 and VOC precursors as input data, it is likely that the decrease of the PAN/ozone and PPN/ozone concentration ratios from morning to mid-afternoon is in part due to thermal decomposition, i.e., an increasing fraction of the PAN and PPN formed is lost as ambient temperature increases. We have noted similar diurnal variations of the PAN/ozone and PPN/ozone in earlier studies carried out in the Los Angeles area, including in Azusa in summer 1993 and summer 1997 (Williams and Grosjean, 1991, Grosjean, et al., 1996, 2001).

8.7 Long-term trends for ozone and PAN in Azusa

Long-term trends for ozone and PAN in Azusa are compared in Figure 8.16. For ozone, the data plotted in Figure 8.16 are the highest one-hour concentrations measured each year from 1979 to 2003. These concentrations exhibit a steady decline, from ca. 400 ppb in the late 70's to ca. 150 ppb in 2003, and can be fit by the regression line shown in Figure 8.16 ($R^2 = 0.91$). For the ten year period 1993 – 2003, during which PAN concentrations have neither increased nor decreased, the regression line that fits the ozone data is not substantially different from that for the entire (1979 – 2003) ozone data set. The regression line for the 1993 – 2003 ozone data is also shown in Figure 8.16. Overall, the results shown in Figure 8.16 indicate that in the last decade the highest one-hour ozone concentrations in Azusa have continued to decline, the highest PAN and PPN have not, and the PAN/ozone and PPN/ozone ratios of highest concentrations have increased by a factor of ca. two. As pointed out in section 7, we stress that the conclusions of our analysis are given with the caveat that PAN and PPN data prior to 2001 are from limited studies of short duration carried out during the smog season.

9. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The results and conclusions presented in this report pertain to Task 3 of work initiated under Contract 99-703 and concluded under a Memorandum of Understanding dated March 20, 2002. To carry out Task 3, we have measured ambient concentrations of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) at one southern California location, Azusa. These measurements have been carried out every 15 minutes between February 2001 and September 2003. For PAN, this study is the longest study carried out in southern California, and the first long-term study in the last ca. 25 years (three long-term studies have been carried out in Riverside in 1966 – 67, 1975 – 76, and 1980). For PPN, this study is the first long-term study of ambient concentrations in southern California. The importance of measuring PAN and PPN and the value of long-term measurements in the context of regulatory policies for ambient air quality are discussed in the article prepared at the completion of Task 2 of this project and need not be repeated here. The article is included as Appendix B to this report.

This report also includes data for perchloroethylene (PCE). PCE was measured every 15 minutes between February 2001 and September 2003, thus yielding ca. 90,000 measurements of ambient PCE along with those of ambient PAN and ambient PPN. We elected to include the PCE data in this report with the hope that long-term time-resolved data for ambient PCE are of value to ARB, as a supplement to other ARB studies of air toxics, to examine the effectiveness of regulatory measures that are being implemented to reduce PCE emissions.

Major findings and conclusions are summarized in sections 9.1 to 9.6. For clarity of presentation, these sections match in contents those of the topics presented in sections 3 – 8 of the report. Tables and figures already included in sections 3 – 8 are not repeated here and are mentioned in sections 9.1 to 9.6 when appropriate. Suggestions and recommendations are made in section 9.7 for additional analysis of the large database obtained in this study, for extracting more information from the raw experimental data, and for future additional work.

9.1 Overview of results

Histograms of all individual measurements indicate that ambient concentrations of PAN, PPN and PCE exhibited lognormal distributions. The PPN/PAN concentration ratios exhibited a normal distribution. PAN concentrations ranged from 0.015 ppb (15 ppt, ppt = part per trillion) to ca. 7.4 ppb in 2001, 6.4 ppb in 2002, and 6.5 ppb in 2003. PPN concentrations ranged from 0.002 ppb (2 ppt) to 0.97 ppb in 2001, 0.83 ppb in 2002, and 0.86 ppb in 2003. PCE concentrations ranged from 0.007 ppb (7 ppt) to ca. 33.2 ppb in 2001, 22.6 ppb in 2002 and 10.9 ppb in 2003. Ambient data for PCE included short-duration events of high concentrations. Time-averaged concentrations (often useful for assessment of human exposure and, for PAN and PPN, of phytotoxicity) are given in Table 3.1 and Table 3.2. The highest 24 hour-averaged concentrations were 2.21 (2001), 1.96 (2002) and 2.45 (2003) ppb for PAN, 0.25 (2001), 0.25 (2002) and 0.31 (2003) ppb for PPN, and 2.14 (2001), 0.87 (2002) and 0.73 (2003) ppb for PCE. The highest monthly-averaged concentrations were 1.20 (2001), 1.16 (2002) and 1.11 (2003) ppb for PAN, 0.13 (2001), 0.14 (2002) and 0.13 (2003) ppb for PPN, and 0.35 (2001), 0.22 (2002) and 0.19 (2003) ppb for PCE. For the PPN/PAN concentration ratio, most values fell into a narrow range of ca. 0.09 – 0.14, although on some instances ratios as low as ca 0.03 and as high as ca. 0.4 were recorded. Monthly–averaged ratios ranged from 0.095 to 0.124 and averaged 0.113 (Table 3.1).

9.2 Average seasonal and diurnal variations

Seasonal and diurnal variations notwithstanding (see below), the data showed no indication that PAN and PPN either increased or decreased between February 2001 and September 2003. In contrast, the frequency of events of high PCE concentrations and the concentrations measured during these events decreased from 2001 to 2002 and decreased again from 2002 to 2003 (Table 4.1).

Average seasonal and average diurnal variations of PAN and PPN were nearly identical. Concentrations increased from winter to summer, and increased from early morning to early afternoon. The concentrations of PAN and PPN measured at the time of the afternoon maximum increased from winter to summer. The study-averaged composite diurnal profile (Figure 4.15) shows a four-fold increase between morning minimum and afternoon maximum (e.g., from 0.4 to 1.6 ppb for PAN), an average interval of ca. 8 hours between morning minimum and afternoon maximum, and an average interval of ca. 16 hours, during which PAN and PPN were nearly constant for ca. 5 hours, between the afternoon maximum and the following morning minimum.

Average seasonal and diurnal variations of PCE were to a large extent influenced by the high PCE events and were higher in winter. Average diurnal variations varied from month to month (and year to year) along with the date and time of day at which high PCE events were recorded. There was little or no association between monthly-averaged concentrations of PCE and those of PAN or PPN ($R^2 = 0.05$). The ratio PAN/PCE of monthly-averaged concentrations was higher in summer and increased, consistent with decreasing PCE concentrations, from 2001 to 2003. PCE concentrations measured every 15 minutes in this study agreed with those measured by ARB in 24-hour samples collected every 12 days.

9.3 Short-term variations

The duration of this study made it possible to examine short-term features. Reflecting changes in emissions and in meteorology, ambient concentrations of PAN, PPN and PCE varied substantially from one day to the next, over periods of a few days, and over shorter periods within a given day.

We examined the high PCE events recorded every 15 minutes and found no coherent patterns. On some days a single event was recorded, while multiple events were recorded on other days. Some high PCE concentrations were recorded at night, others in the morning, and others in the afternoon. As mentioned above, the frequency and magnitude of these high PCE events decreased between 2001 and 2003. This decreasing trend is likely to result from current regulatory measures whose objective is to reduce stationary source emissions of PCE from dry cleaning, degreasing and other operations.

For PAN and PPN, short-term features described and illustrated in section 5 of this report include the variations of the time of the afternoon maximum, the occurrence of several PAN (PPN) maxima in the afternoon and evening on the same day, the occurrence of secondary PAN (PPN) maxima in the late night and early morning hours, and the occurrence of episodes of high PAN (PPN) concentrations outside of the traditional smog season. We also examined periods during which PAN, PPN and PCE were "flat" for several hours (during daytime and at night) and periods during which PCE was "flat" but PAN and PPN were not.

We examined the overall data according to day of the week, and found that PAN and PPN concentrations were on average highest on Sunday and second highest on Saturday (see for example Figure 5.1 for PAN in 2002). The opposite was observed for PCE, which on average was lowest between Saturday evening and Monday morning (e.g., Figure 5.3). Using data for 2002 as an example, the Sunday/other day concentration ratio ranged from 1.04 (Saturday) to 1.25 (Tuesday) for PAN and from 0.54 (Thursday) to 0.76 (Monday) for PCE. For PCE, day-of-the-week changes in concentrations reflect day-of-the-week changes in activities, i.e., less PCE is being emitted between Saturday evening and Monday morning. For PAN and PPN, the "week-end" effect identified in this long-term study is likely to result, as has been well documented for ozone, from changes in the magnitude and timing of emissions of precursors, i.e., NO_X and the VOC whose in-situ oxidation lead to PAN and PPN.

9.4 PPN/PAN concentration ratio

This study included the first long-term measurements of PPN in southern California and we examined the PPN/PAN concentration ratio in some detail. The histogram of all individual ratios exhibited a narrow normal distribution centered at ca. 0.12. The few episodes with higher (ca. 0.4) and lower (ca. 0.03) PPN/PAN ratios occurred in the evening or at night. The close association between ambient concentrations of PPN and those of PAN was reflected in similar average seasonal and diurnal variations, highly correlated plots of log PPN vs. log PAN for all individual measurements ($R^2 > 0.98$), a narrow range of monthly-averaged concentration ratios (e.g., range = 0.095 – 0.124 and study average = 0.113 for PPN/PAN) and a high degree of correlation in least squares linear regressions of concentrations of PPN vs. those of PAN and vice versa (Table 6.1). Thus, regression slopes (Y = PPN, X = PAN) ranged from 0.108 to 0.131 and averaged 0.119 in 2001, 0.124 in 2002, 0.122 in 2003 and 0.122 for the entire study. Regression slopes did not exhibit a seasonal trend but the corresponding intercepts did, e.g., intercepts in regressions of PAN vs. PPN were higher in summer.

Although the PPN/PAN concentration ratio varied little with time of day, average diurnal variations included two maxima (one at night and the other in the afternoon) and two minima (one in the morning and the other in the evening). The afternoon maximum was higher in summer, lower in winter, and lower overall than the nighttime maximum (e.g., Figure 6.11). The afternoon maximum of the PPN/PAN concentration ratio occurred generally later than the afternoon peak in PAN and PPN concentrations.

The two minima defined how the PPN/PAN concentration ratio varies with the PAN and PPN concentrations. Between morning minimum and evening minimum, the PPN/PAN concentration ratio varies in the same direction as the concentrations, first increasing with increasing PAN and PPN until the afternoon maximum and then decreasing with decreasing PAN and PPN between afternoon maximum and evening minimum. Between evening minimum and morning minimum, the PPN/PAN concentration ratio varies in the direction opposite of that of the concentrations, first increasing with decreasing PAN and PPN until the nighttime maximum of the PPN/PAN ratio and then decreasing while concentrations increase. This cycle of co-variations and opposite variations is summarized in Figure 5.24, which shows a scatterplot of the PPN/PAN ratios vs. PPN concentrations for 2003.

Having shown that both PAN and PPN were on average higher on weekends than on weekdays, we examined the PPN/PAN concentration ratio for each day of the week. The PPN/PAN ratio shows little difference overall between weekdays and weekends. There were, however, day of the week differences in the relative magnitude of the nighttime and afternoon maxima.

Also discussed qualitatively in section 6 are the formation and removal processes of PAN and PPN and how these processes affect the ambient PPN/PAN concentration ratio. Removal of PAN involves thermal decomposition and photolysis. Removal of PPN involves thermal decomposition, photolysis and reaction with OH. Removal by photolysis is negligible for both PAN and PPN, and removal of PPN by reaction with OH can be neglected for air mass transport times relevant to Azusa. Thermal decomposition is a major loss process for both PAN and PPN. Thermal decomposition loss rates are of the same magnitude, and therefore the ambient PPN/PAN concentration ratio is not controlled by loss processes but by differences in formation processes. Formation of PAN and formation of PPN depend on both air parcel transport time and the mix of VOC precursors. In the simplest case of a constant mix of VOC precursors, transport time is important since VOC that are precursors to PPN are on average more reactive than VOC that are precursors to PAN, i.e., the ambient PPN/PAN concentration ratio is higher in less aged air masses. The mix of VOC precursors is rarely constant and changes with, for example, fuel composition (exhaust and evaporative emissions), pattern in vehicle traffic (e.g., cold start and hot-stabilized emissions are different in magnitude and in speciated VOC profiles), and/or contribution of biogenic VOC (summer > winter; also day > night) that are precursors to PAN (e.g., isoprene) and/or to PPN (e.g., cis-3-hexen-ol).

As a result of the interplay between meteorology and changes in VOC emission profiles, the ambient PPN/PAN concentration could vary substantially with time of day. Indeed, we have recorded on occasion episodes of low and high PPN/PAN concentration ratios that span ca. one order of magnitude, i.e., from ca. 0.03 to ca. 0.4. However, the great majority of PPN/PAN ratios fell within a narrow range centered at ca. 0.12, a remarkable feature if one considers all the factors that may affect this ratio.

9.5 Long-term trends

Grosjean (2003; Appendix B to this report) has examined long-term trends in ambient PAN and ambient PPN measured at southern California locations between 1960 and 1997. We added our results for 2001, 2002 and 2003 to the historical record. While ambient levels of peroxyacyl nitrates have declined substantially since 1960, that data from this study indicate that PAN and PPN measured in 2001 – 2003 are about the same as those measured in the short-term summer studies carried out in 1993 (at 4 locations including Azusa) and 1997 (at 2 locations including Azusa). Before that, PAN (but not PPN) was last measured in 1987 at several southern California locations (again including Azusa), and the concentrations measured in 1987 were ca. twice as high as those measured in 1993, 1997, and 2001 – 2003. Thus, with the caveat that only limited data are available, it appears that the ambient concentration ratio has not changed much, if any, during the decade 1993 – 2003. During that decade, there have been important changes in emission in vehicle fuel composition (and presumably in VOC emissions from mobile sources), including the introduction of California Phase 2 reformulated gasolines in 1996 and the phasing out of MTBE, which took place progressively in 2003 while this study was being carried out.

9.6 Comparison of ambient PAN, PPN and ozone

On average, diurnal variations of PAN and PPN follow closely those of ozone, with concentrations increasing from early morning to mid-afternoon and decreasing thereafter. However, concentrations of PAN and PPN do not correlate with those of ozone measured at the same time. These two observations also apply to daily maxima PAN (PPN) and daily maxima ozone, which on average coincide with respect to time of occurrence but whose concentrations correlate poorly with each other. The PAN/ozone concentration ratio shows substantial variability from day to day, with no apparent seasonal trend. However, the PAN/ozone concentration ratio on averages shows well-defined diurnal variations (Figure 8.15) and decreases from early morning to mid-afternoon, increases from mid-afternoon to evening, and decreases again at night. The decrease from early morning to mid-afternoon, which we have observed in earlier studies, is in part due to an increase in the thermal decomposition of PAN and PPN during daytime hours.

A comparison of long-term trends in ambient ozone, PAN and PPN in Azusa indicates that, in contrast to PAN and PPN whose concentrations have not changed substantially in the decade 1993 – 2003 (section 7), peak ozone concentrations have continued to decrease during that decade at a "rate" consistent with that observed since the late 1970's. Thus, with the caveat that the PAN and PPN data record is incomplete, highest PAN (PPN) / highest one-hour ozone concentration ratios have increased in the last decade by a factor of ca. two.

9.7 Recommendations

Our recommendations fall into three categories, namely additional interpretation of the comprehensive database available from this study, additional "mining" of the raw experimental data, and suggestions for future work.

With respect to additional interpretation of the data, we would like to expand, using the 2001 – 2003 data, on earlier and limited work (see Appendix A) we have done to (a) calculate the amount of PAN and PPN loss by thermal decomposition and (b) carry out more in-depth studies of the relationships between PAN, PPN and their VOC precursors. These two topics cannot be examined using our database alone, i.e., NO, NO_2 and temperature data are needed to calculate thermal decompositions, and meteorology and VOC data (hydrocarbons and carbonyls) are needed to examine, with and without modeling, relationships between PAN, PPN and the speciated VOC from which their form (PAMS data, although limited to summer and lacking detailed information on carbonyls, would be suitable as a starting point). For PCE, we would like to explore in more detail, using data for CO, meteorology and other indicators as appropriate, the contribution of local (Azusa), nearby and more distant sources to ambient PCE, with emphasis on the high PCE events recorded in this study.

With respect to additional "mining" of our raw experimental data, the chromatograms of ambient air from this study also contain information on peroxyacyl nitrates other than PAN and PPN. These compounds include, tentatively, the unsaturated compounds APAN and MPAN and saturated higher molecular weight compounds such as PiBN and/or PnBN. APAN, first identified recently in Japan (Tanimoto and Akimoto, 2001), has also been measured in Houston in 2000 (Roberts et al., 2001) but to our knowledge, never in California. MPAN, which we have measured at Tanbark Flat in 1989 – 91 (Grosjean, et al 1993a), forms from the biogenic hydrocarbon isoprene and its oxidation product methacrolein. We have also measured PnBN at Tanbark Flat in 1989 – 91 (Grosjean, et al, 1993b). Only a modest effort would be necessary to synthesize authentic standards (as we have done before) for positive identification, to use these standards to construct calibration curves, and to use these calibration curves to calculate ambient concentrations of APAN, MPAN, PiBN, and PnBN for 2001 – 2003.

Suggestions for future work include additional long-term measurements of peroxyacyl nitrates and of speciated VOC at one location in southern California. Long-term series of measurements are of great value for regulatory purposes. Long-term measurements of PAN and PPN have been carried out, and continue to be, in other urban areas and at rural and remote locations, in the U.S. and elsewhere. Only modest support, e.g., less than $100K per year, would be required to measure PAN and PPN at one location, e.g., Azusa. With respect to speciated VOC, we still lack the year-around, long-term ambient data that are critically important to assess the effectiveness of emission control programs. In the case of our study alone, it is difficult to examine PPN and PAN in a more in-depth manner when no information is available regarding long-term patterns of speciated VOC in the source-dominated region of the South Coast Air Basin. Speciated VOC (ca. 80 speciated hydrocarbons and a full suite of ca. 60 speciated carbonyls, not just the few carbonyls reported in summer as part of PAMS) could be best measured at a central location (e.g., downtown Los Angeles), and at a modest frequency (e.g., one set of samples per week, e.g., 6 – 9 a.m. on a week day). Again, only modest financial support, comparable to that estimated above for long-term measurements of PAN, would be needed to implement such a valuable long-term monitoring program.

10. REFERENCES

Croes, B.E.; Dolislager, L.J.; Larsen, L.C.; Pitts, J.N. (2003). Environmental Monitor (published by Air Waste Manag. Assoc.), July, 27 – 35

Grosjean, D.; Williams II, E.L.; Grosjean, E. (1993a). Environ. Sci. Technol. 27, 110 – 121.

Grosjean, D.; Williams II, E.L.; Grosjean, E. (1993b). Environ. Sci. Technol. 27, 326 – 331.

Grosjean, E.; Grosjean, D.; Fraser, M.P.; Cass, G.R. (1996). Environ. Sci. Technol., 30, 2704 – 2714.

Grosjean, E.; Grosjean, D.; Woodhouse, L.F. (2001). Environ. Sci. Technol., 35, 4007 – 4014.

Grosjean, D. (2003). Atmos. Environ., 37, Supplement 2, S221 – S238.

Pitts Jr., J.N.; Grosjean, D (1979). Report ARB-R-5-384-79-100 to California Air Resources Board, Sacramento, CA, Contracts 5-384 and A6-171-30. National Technical Information Service PB-301294/5WP, Springfield, VA

Roberts, J.M., et al. (2001). Geophys. Res. Letters, 28, 4195 – 4198.

Tanimoto, H.; Akimoto, H. (2001). Geophys. Res. Letters, 28, 2831 –2834.

Taylor, O.C. (1969). J. Air Pollut. Control Assoc., 19, 347 – 351.

Temple, P.J.; Taylor, O.C. (1983). Atmos. Environ., 17, 1583 – 1587.

Williams II, E.L.; Grosjean, D. (1990). Atmos. Environ., 24A, 2369 – 2377.

Williams II, E.L.; Grosjean, D. (1991). Environ. Sci. Technol. 25, 653 – 659.

Table 2.1 PAN analyzer service and calibration logsheet				
DGA PAN SERVICE/CALIBRATION LOG SHEET				
Instrument: PAN GC-ECD #2 SRI# N3250				
Column:15m*.53mm id*1umdf Rtx 200MS #2 01/26/2001				
LOCATION	AZUSA	AZUSA	AZUSA	AZUSA
DATE(mmddyy)	07/29/03	07/29/03	07/29/03	07/29/03
TIME (pst)	18:32	19:17	20:15	21:35
OPERATOR	EG	EG	EG	EG
UHP Nitrogen Cylinder				
Date Installed	06/05/2003			########
REG Stage 1(psi)	1150			1150
REG Stage 2(psi)	30			30
N2 usage,psi/day	25			
N2 Cyl #	cyl 10			cyl 10
UOP N2 Puifier	cyl 2			cyl 2
SRI 8610C Gas Chromatograph				
Carrier 1 Setpoint	6			6
Carrier 1 Actual	5			5
ECD Current Setpoint	800			800
ECD Current Actual	800			800
Valve T Setpoint	25			25
Valve T Actual	30			30
ECD Cell T Setpoint	56			56
ECD Cell T Actual	60			60
Column Oven 1 T Setpoint	29			29
Column Oven 1 T Actual	30			30
Valve switching?	✓			✓
Valve in correct position?	✓			✓
Sample Pump				
Pump on audibly?	✓			✓
Vacuum pump interface light on?	✓			✓
ROOF				
Teflon Filter Changed	✓			
Sample Flow, cc/min(load)	425 FM			
Sample Flow, cc/min(inject)	475 FM			
Data System				
Baseline,mv	-8.5			
PCE Tr			1.42-1.43	
PAN Tr	1.80			1.80
PPN Tr		3.32	3.32	
Air peak height, mv	3332			
Sample Frequency	15 min			
Check computer time (pst)	✓			
Check file time vs. computer	✓			
Copy Files to C Drive	✓			
Copy Files to CDRW	✓			
Room Conditions	67F			
Weather conditions	82F clouds/sprinkles			
Table 2.1 PAN analyzer service and calibration logsheet continued				

CALIBRATION				
Zero Air	DGA pag zero air			**Indoors**
n	3			**Loss**
Zero Air response, Peak Height,mv	0		**ROOF**	**Rate**
	PAN	PPN	PPN	PAN
PAN synthesized,date	07/23/2003	07/23/2003	07/23/2003	#######
PAN, ppbv	15.2	15.4	15.4	15.2
n	5	4	6	4
PAN response, Peak Height,mv	834.7	566.4	538.4	806.6
PAN response, Peak Area	5901	6474	6097	5651
PAN,rf, mv/ppbv	54.9	36.8	35.0	53.1
PAN,rf, area/ppbv	388.2	420.4	395.9	371.8
	heated tube 166C	heated tube 165C	**PPN Indoors Post Roof**	
PAN, ppbv	15.2	15.4	15.4	
n	2	2	4	
PAN response, Peak Height,mv	4.6	5.6	542.1	
PAN response, Peak Area	49.2	60.7	6196	
PAN,rf, mv/ppbv	0.3	0.4	35.2	
PAN,rf, area/ppbv	3.2	3.9	402.3	
PAN Heated tube % decrease	99.45	99.01		
PCE, tank			Large Tank	
PCE, ppbv			4.96	
n			6	
PCE response, Peak Height,mv			474	
PCE response, Peak Area			3053	
PCE,rf, mv/ppbv			95.6	
PCE,rf, area/ppbv			615.5	
PCE, psi			1010	
EXTRA				
Column flow, cc/min	16.4			
ECD makeup flow, cc/min	40.0			
Total flow, cc/min(load)	56.4			
Total flow, cc/min(inject)	56.4			
Flow at GC Inlet				
Sample Flow, cc/min(load)	425 FM			
Sample Flow, cc/min(inject)	475 FM			

Table 3.1a Summary of ambient concentrations of PAN,PPN and PCE, Azusa, February 2001-September 2003											
	F-01	M-01	A-01	M-01	J-01	J-01	A-01	S-01	O-01	N-01	D-01
PCE ppbv											
AVERAGE	0.089	0.316	0.313	0.231	0.202	0.187	0.216	0.274	0.353	0.246	0.180
STDEV	0.064	1.218	1.071	0.243	0.142	0.133	0.154	0.309	0.896	0.362	0.453
RSD %	71	385	343	105	70	71	71	113	254	147	252
MIN	0.016	0.011	0.010	0.009	0.017	0.021	0.027	0.027	0.020	0.008	0.009
MAX	0.437	25.283	32.303	5.676	1.895	1.599	2.302	8.153	33.146	11.112	15.434
PAN ppbv											
AVERAGE	0.081	0.738	0.770	1.195	1.001	1.009	1.120	0.990	1.026	0.634	0.308
STDEV	0.035	0.656	0.655	0.830	0.925	0.826	1.004	0.736	0.768	0.536	0.208
RSD %	44	89	85	69	92	82	90	74	75	85	67
MIN	0.027	0.018	0.033	0.168	0.043	0.025	0.042	0.026	0.020	0.056	0.015
MAX	0.263	4.359	3.714	4.776	6.919	6.083	7.392	4.486	3.793	2.850	1.490
PPN ppbv											
AVERAGE	0.009	0.073	0.081	0.129	0.108	0.114	0.129	0.117	0.125	0.076	0.034
STDEV	0.003	0.071	0.074	0.098	0.110	0.100	0.124	0.091	0.099	0.066	0.025
RSD %	31	98	91	76	102	88	96	77	80	87	72
MIN	0.004	0.002	0.003	0.017	0.004	0.003	0.005	0.002	0.002	0.006	0.002
MAX	0.019	0.515	0.431	0.601	0.896	0.825	0.970	0.569	0.504	0.353	0.196
PPN/PAN											
AVERAGE	0.115	0.095	0.102	0.105	0.104	0.110	0.111	0.119	0.120	0.118	0.112
STDEV	0.028	0.012	0.009	0.009	0.012	0.011	0.014	0.019	0.015	0.015	0.027
RSD %	24	12	9	8	12	10	13	16	13	13	24
MIN	0.063	0.059	0.067	0.081	0.064	0.064	0.034	0.081	0.079	0.067	0.070
MAX	0.233	0.171	0.146	0.148	0.176	0.211	0.191	0.286	0.179	0.209	0.419
PCE/PAN	1.102	0.429	0.406	0.193	0.202	0.186	0.193	0.277	0.344	0.388	0.583
COUNT	628	2948	2873	2472	2781	2954	2893	2823	2908	2850	2955
TOTAL # OF 15 MIN	628	2976	2880	2976	2880	2976	2976	2880	2976	2880	2976
% DATA CAPTURE	100	99	100	83	97	99	97	98	98	99	99

Table 3.1b Summary of ambient concentrations of PAN,PPN and PCE, Azusa, February 2001-September 2003												
	J-02	F-02	M-02	A-02	M-02	J-02	J-02	A-02	S-02	O-02	N-02	D-02
PCE ppbv												
AVERAGE	0.171	0.220	0.131	0.141	0.141	0.138	0.149	0.166	0.194	0.159	0.145	0.116
STDEV	0.183	0.643	0.143	0.174	0.315	0.133	0.164	0.131	0.178	0.117	0.193	0.128
RSD %	107	293	109	124	223	97	111	79	92	74	133	110
MIN	0.010	0.011	0.013	0.014	0.014	0.018	0.017	0.023	0.014	0.013	0.008	0.009
MAX	2.131	22.557	2.228	3.114	9.516	2.653	2.853	1.719	2.687	1.789	4.483	2.761
PAN ppbv												
AVERAGE	0.421	0.635	0.573	0.747	0.905	1.065	0.949	1.160	0.906	1.115	0.510	0.413
STDEV	0.283	0.496	0.472	0.654	0.588	0.816	0.891	0.782	0.691	0.606	0.484	0.264
RSD %	67	78	82	88	65	77	94	67	76	54	95	64
MIN	0.040	0.052	0.028	0.054	0.041	0.094	0.018	0.084	0.032	0.159	0.024	0.049
MAX	1.722	2.941	4.684	4.653	3.918	4.875	6.385	4.506	3.819	4.320	3.326	1.890
PPN ppbv												
AVERAGE	0.051	0.079	0.065	0.080	0.102	0.125	0.113	0.140	0.108	0.127	0.060	0.049
STDEV	0.035	0.066	0.056	0.076	0.073	0.105	0.115	0.101	0.085	0.076	0.061	0.032
RSD %	69	83	85	96	72	84	102	72	79	60	100	66
MIN	0.005	0.006	0.003	0.004	0.005	0.008	0.002	0.007	0.004	0.020	0.003	0.004
MAX	0.234	0.398	0.552	0.607	0.538	0.643	0.827	0.628	0.487	0.543	0.419	0.235
PPN/PAN												
AVERAGE	0.122	0.122	0.112	0.102	0.109	0.112	0.113	0.118	0.119	0.113	0.115	0.119
STDEV	0.016	0.016	0.012	0.011	0.011	0.011	0.015	0.015	0.015	0.013	0.016	0.016
RSD %	13	13	11	11	10	10	13	12	12	12	14	13
MIN	0.070	0.073	0.077	0.066	0.063	0.069	0.063	0.042	0.086	0.073	0.067	0.076
MAX	0.276	0.240	0.154	0.132	0.149	0.155	0.173	0.164	0.217	0.192	0.183	0.194
PCE/PAN	0.406	0.346	0.229	0.188	0.156	0.130	0.157	0.143	0.215	0.142	0.284	0.280
COUNT	2968	2635	2839	2826	2926	2842	2957	2944	1982	2628	2854	2941
TOTAL # OF 15 MIN	2976	2688	2976	2880	2976	2880	2976	2976	2880	2976	2880	2976
% DATA CAPTURE	99.7	98.0	95.4	98.1	98.3	98.7	99.4	98.9	68.8	88.3	99.1	98.8

Table 3.1c Summary of ambient concentrations of PAN,PPN and PCE, Azusa, February 2001-September 2003													
	J-03	**F-03**	**M-03**	**A-03**	**M-03**	**J-03**	**J-03**	**A-03**	**S-03**		**AVE**	**MIN**	**MAX**
PCE ppbv										**PCE ppbv**			
AVERAGE	0.194	0.084	0.117	0.058	0.109	0.088	0.115	0.118	0.152	**AVERAGE**	0.172	0.058	0.353
STDEV	0.331	0.090	0.179	0.081	0.152	0.078	0.093	0.110	0.186	**STDEV**		0.064	1.218
RSD %	171	107	153	138	140	89	81	93	123	**RSD %**		70	385
MIN	0.007	0.007	0.008	0.008	0.007	0.010	0.010	0.008	0.019	**MIN**		0.007	0.027
MAX	10.873	1.077	3.587	1.436	2.119	1.117	0.965	1.987	4.470	**MAX**		0.437	33.15
PAN ppbv										**PAN ppbv**			
AVERAGE	0.332	0.440	0.670	0.491	1.041	1.106	1.057	0.800	1.087	**AVERAGE**	0.790	0.081	1.19
STDEV	0.232	0.295	0.518	0.349	0.843	0.939	0.955	0.756	0.941	**STDEV**		0.035	1.00
RSD %	70	67	77	71	81	85	90	95	87	**RSD %**		44	95
MIN	0.044	0.024	0.036	0.022	0.037	0.111	0.027	0.026	0.017	**MIN**		0.015	0.168
MAX	1.456	1.573	3.163	1.927	5.368	5.994	5.173	5.960	6.499	**MAX**		0.263	7.39
PPN ppbv										**PPN ppbv**			
AVERAGE	0.041	0.050	0.080	0.055	0.123	0.124	0.125	0.094	0.126	**AVERAGE**	0.091	0.009	0.14
STDEV	0.029	0.035	0.065	0.040	0.108	0.119	0.117	0.094	0.114	**STDEV**		0.003	0.12
RSD %	72	70	81	72	88	96	93	100	90	**RSD %**		31	102
MIN	0.005	0.003	0.003	0.002	0.003	0.009	0.003	0.003	0.002	**MIN**		0.0017	0.0198
MAX	0.187	0.197	0.401	0.225	0.792	0.779	0.685	0.741	0.860	**MAX**		0.019	0.97
PPN/PAN										**PPN/PAN**			
AVERAGE	0.124	0.111	0.116	0.111	0.112	0.106	0.117	0.114	0.115	**AVERAGE**	0.113	0.095	0.124
STDEV	0.026	0.016	0.013	0.010	0.013	0.011	0.013	0.015	0.016	**STDEV**		0.009	0.03
RSD %	21	14	11	9	12	10	11	13	14	**RSD %**		8	24
MIN	0.052	0.046	0.059	0.079	0.068	0.073	0.077	0.026	0.049	**MIN**		0.026	0.086
MAX	0.315	0.194	0.170	0.155	0.153	0.144	0.207	0.163	0.178	**MAX**		0.132	0.42
PCE/PAN	0.583	0.191	0.174	0.119	0.105	0.079	0.109	0.148	0.140				
COUNT	2931	2636	2931	2844	2958	2864	2898	2914	2193	**COUNT TOTAL**	87596		
TOTAL # OF 15 MIN	2976	2688	2976	2880	2976	2880	2976	2976	2304	**TOTAL # OF 15 MIN**			
% DATA CAPTURE	98	98	98	99	99	99	97	98	95	**% DATA CAPTURE**	96.7	68.8	100.0

Table 4.1a List of days and times ambient PCE concentrations exceeded 2.0 ppbv

Date	Time, pst	PCE, ppbv	Date	Time, pst	PCE, ppbv	Date	Time, pst	PCE, ppbv	Date	Time, pst	PCE, ppbv
2001											
3/18/01	3:15	2.18	4/10/01	11:15	2.25	4/29/01	18:45	4.58	10/26/01	6:00	3.66
3/18/01	3:30	2.15	4/10/01	12:45	2.63	4/29/01	19:00	6.43	10/26/01	6:45	18.96
3/18/01	7:00	2.44	4/10/01	14:30	2.41	4/29/01	19:45	2.72	10/26/01	7:00	3.31
3/18/01	7:15	2.29	4/10/01	15:00	2.39	4/29/01	20:00	2.73	10/26/01	7:30	33.15
3/18/01	7:30	2.99	4/10/01	16:00	3.22	5/2/01	18:45	2.63	10/26/01	7:45	20.97
3/18/01	7:45	4.59				5/3/01	8:15	2.38	10/26/01	8:00	3.05
3/18/01	18:15	2.19	4/11/01	9:15	2.20	5/6/01	6:30	3.95	10/26/01	8:30	6.88
			4/11/01	11:30	2.22	5/7/01	21:00	5.68	10/26/01	17:15	3.81
3/30/01	20:15	11.84	4/11/01	12:15	3.11	5/8/01	6:15	2.40	11/7/01	20:30	2.61
3/30/01	20:30	23.97	4/11/01	12:45	2.41	5/8/01	23:45	2.70	11/14/01	21:30	10.32
3/30/01	20:45	21.60	4/11/01	22:15	2.12	5/9/01	0:45	2.08	11/29/01	4:15	11.11
3/30/01	21:00	4.90	4/12/01	13:30	2.34	8/14/01	4:00	2.30	11/30/01	8:15	3.10
3/30/01	21:15	9.20	4/15/01	12:00	2.09	9/4/01	21:30	2.88	11/30/01	16:45	3.43
3/30/01	21:30	16.66	4/22/01	21:00	2.29	9/14/01	19:00	2.28	12/1/01	9:00	4.85
3/30/01	21:45	15.43	4/23/01	2:30	2.95	9/24/01	23:15	2.89	12/1/01	22:00	15.43
3/30/01	22:00	5.69	4/25/01	7:45	3.08	9/25/01	1:30	2.09	12/1/01	22:15	2.34
3/30/01	22:15	6.40	4/28/01	11:15	8.93	9/25/01	6:45	4.09	12/2/01	0:30	10.75
3/30/01	22:30	2.68	4/28/01	11:45	2.58	9/25/01	7:00	3.05	12/2/01	0:45	6.99
3/30/01	22:45	3.85	4/28/01	17:00	3.31	9/25/01	8:15	2.14	12/2/01	1:00	3.44
3/30/01	23:00	2.95	4/28/01	17:15	8.56	9/29/01	23:00	3.50	12/2/01	1:45	3.38
3/30/01	23:15	12.01	4/28/01	17:30	3.93	9/29/01	23:15	8.15	12/2/01	2:00	3.08
3/30/01	23:30	25.28				10/3/01	0:15	3.64	12/2/01	7:30	6.36
3/30/01	23:45	17.92	4/29/01	10:15	3.29	10/10/01	18:45	2.92	12/2/01	9:30	3.65
3/31/01	0:00	18.51	4/29/01	11:00	12.02	10/12/01	7:45	2.32	12/2/01	14:00	3.51
3/31/01	0:15	19.56	4/29/01	11:15	3.97	10/12/01	8:00	2.07	12/19/01	19:30	2.56
3/31/01	0:30	8.51	4/29/01	11:30	2.42	10/12/01	9:45	4.56			
3/31/01	0:45	22.91	4/29/01	11:45	32.30	10/12/01	10:00	3.81			
3/31/01	1:00	4.48	4/29/01	12:00	7.81	10/18/01	8:00	4.77			
3/31/01	1:30	2.53	4/29/01	14:30	21.76	10/19/01	10:45	4.24			
			4/29/01	14:45	12.52	10/25/01	23:30	2.37			
4/2/01	20:30	4.25	4/29/01	15:00	5.26	10/26/01	0:00	3.21			
4/2/01	20:45	3.53	4/29/01	15:15	4.67	10/26/01	0:45	2.34			
4/8/01	22:15	2.65	4/29/01	15:30	3.54	10/26/01	1:00	2.26			
4/9/01	11:15	8.08	4/29/01	16:00	2.84	10/26/01	1:15	2.18			
4/9/01	11:30	2.19	4/29/01	16:30	3.06	10/26/01	1:30	2.02			
4/9/01	11:45	4.10	4/29/01	16:45	3.93	10/26/01	1:45	2.14			
4/9/01	16:00	3.66	4/29/01	17:00	12.75	10/26/01	2:00	3.24			
4/9/01	16:15	2.02	4/29/01	17:15	5.03	10/26/01	2:15	2.54			
4/9/01	17:15	2.25	4/29/01	17:30	15.70	10/26/01	2:30	7.00			
4/9/01	17:45	2.31	4/29/01	17:45	2.72	10/26/01	2:45	7.52			
4/9/01	18:15	3.38	4/29/01	18:00	13.32	10/26/01	3:00	3.34			
4/9/01	18:45	2.10	4/29/01	18:15	6.89	10/26/01	3:15	2.59			
4/9/01	19:00	3.22	4/29/01	18:30	10.07	10/26/01	3:30	2.63			

Table 4.1b List of days and times ambient PCE concentrations exceeded 2.0 ppbv

Date	Time, pst	PCE, ppbv	Date	Time, pst	PCE, ppbv
2002			**2003**		
1/24/02	7:45	2.13	1/12/03	0:45	2.92
2/3/02	1:45	5.50	1/13/03	0:45	3.48
2/3/02	2:30	6.35	1/14/03	8:30	10.87
2/3/02	9:30	2.48	1/14/03	11:00	3.86
			1/14/03	16:45	4.19
2/5/02	6:00	13.99	1/14/03	17:15	3.09
2/5/02	6:15	12.64	1/18/03	7:15	2.58
			1/20/03	2:00	2.32
2/7/02	2:30	3.02	1/24/03	8:15	2.16
2/7/02	4:30	3.67	1/29/03	2:45	2.90
2/7/02	5:15	22.56	1/30/03	1:15	2.14
2/7/02	5:30	4.59	3/9/03	8:00	2.62
2/7/02	5:45	2.87	3/11/03	4:45	3.40
2/7/02	8:30	2.47	3/12/03	10:00	3.59
2/24/02	14:30	4.16	5/13/03	18:00	2.12
3/5/02	19:15	2.23	9/5/03	7:15	3.54
3/27/02	1:30	2.19	9/21/03	8:00	2.25
4/9/02	23:15	2.41	9/22/03	6:15	4.47
4/15/02	15:15	3.02			
4/23/02	12:30	2.88			
4/23/02	12:45	3.11			
4/28/02	17:30	2.69			
5/4/02	12:45	9.52			
5/4/02	13:00	3.41			
5/4/02	13:45	6.75			
5/4/02	14:00	3.12			
5/11/02	18:00	4.15			
5/11/02	18:15	7.84			
5/30/02	20:15	5.14			
6/4/02	16:15	2.65			
7/2/02	0:15	2.85			
7/30/02	6:45	2.21			
9/5/02	18:15	2.69			
9/5/02	19:45	2.12			
9/5/02	21:00	2.03			
11/28/02	7:15	4.48			
12/4/02	8:15	2.76			

Table 4.2 Comparison of ambient PCE concentraions measured every 15 minutes vs. those measured by the ARB in 24-hour samples.					
Date	PCE, ppbv		Concentration ratio	Concentration difference, ppbv	RSD, percent
	ARB(a)	DGA(b)	DGA/ARB	DGA-ARB	
03/08/2001	0.17	0.22	1.29	0.05	18
03/20/2001	0.32	0.46	1.43	0.14	25
04/01/2001	0.15	0.21	1.37	0.06	22
04/13/2001	0.22	0.28	1.28	0.06	18
04/25/2001	0.23	0.36	1.56	0.13	31
05/07/2001	0.23	0.33	1.43	0.10	25
05/19/2001	0.10	0.12	1.18	0.02	12
06/12/2001	0.09	0.13	1.42	0.04	24
06/24/2001	0.11	0.13	1.19	0.02	13
07/06/2001	0.15	0.21	1.42	0.06	25
07/14/2001	0.04	0.15	3.78	0.11	82
07/30/2001	0.12	0.15	1.22	0.03	14
08/11/2001	0.15	0.20	1.32	0.05	20
08/23/2001	0.13	0.19	1.49	0.06	28
09/04/2001	0.17	0.22	1.32	0.05	19
09/16/2001	0.13	0.17	1.31	0.04	19
09/28/2001	0.40	0.47	1.17	0.07	11
10/10/2001	0.28	0.35	1.24	0.07	15
10/22/2001	0.13	0.17	1.34	0.04	20
11/03/2001	0.23	0.28	1.24	0.05	15
01/02/2002	0.25	0.29	1.17	0.04	11
01/14/2002	0.22	0.26	1.17	0.04	11
01/26/2002	0.24	0.23	0.94	-0.01	4
02/07/2002	0.92	0.87	0.94	-0.05	4
02/19/2002	0.15	0.15	1.01	0.00	1
03/03/2002	0.06	0.05	0.78	-0.01	17
03/15/2002	0.05	0.06	1.29	0.01	18
03/27/2002	0.17	0.22	1.27	0.05	17
04/08/2002	0.07	0.08	1.16	0.01	10
04/20/2002	0.06	0.05	0.91	-0.01	7
05/02/2002	0.07	0.08	1.16	0.01	10
05/26/2002	0.04	0.04	1.03	0.00	2
06/19/2002	0.09	0.11	1.23	0.02	15
07/01/2002	0.11	0.13	1.18	0.02	12
07/13/2002	0.09	0.11	1.26	0.02	16
07/25/2002	0.27	0.30	1.12	0.03	8
08/06/2002	0.16	0.21	1.33	0.05	20
08/18/2002	0.05	0.05	1.07	0.00	5
08/30/2002	0.15	0.17	1.15	0.02	10
09/11/2002	0.14	0.17	1.25	0.03	16
10/05/2002	0.20	0.23	1.15	0.03	10
10/17/2002	0.10	0.11	1.13	0.01	9
10/29/2002	0.08	0.10	1.31	0.02	19
11/28/2002	0.07	0.10	1.43	0.03	25
12/04/2002	0.19	0.22	1.17	0.03	11
12/16/2002	0.06	0.07	1.21	0.01	13
12/28/2002	0.06	0.07	1.24	0.01	15
01/09/2003	0.14	0.16	1.14	0.02	9
02/02/2003	0.03	0.03	1.03	0.00	2
02/14/2003	0.08	0.10	1.21	0.02	13
02/26/2003	0.05	0.07	1.34	0.02	21
03/10/2003	0.16	0.16	1.03	0.00	2
03/22/2003	0.13	0.15	1.12	0.02	8
04/15/2003	0.04	0.04	1.05	0.00	3
04/27/2003	0.05	0.06	1.22	0.01	14
05/09/2003	0.06	0.05	0.82	-0.01	14
05/21/2003	0.29	0.33	1.14	0.04	9
06/02/2003	0.07	0.08	1.07	0.01	5
06/14/2003	0.14	0.16	1.15	0.02	10
06/26/2003	0.13	0.17	1.27	0.04	17
07/08/2003	0.08	0.10	1.21	0.02	14
07/20/2003	0.06	0.06	1.06	0.00	4
08/01/2003	0.06	0.06	0.97	0.00	2
08/13/2003	0.13	0.16	1.26	0.03	16
08/25/2003	0.08	0.10	1.26	0.02	16
09/06/2003	0.16	0.18	1.14	0.02	9
09/18/2003	0.11	0.12	1.13	0.01	8
AVE	0.145	0.175	1.234	0.030	14.5
STDEV	0.123	0.130	0.350	0.032	10.9
MIN	0.030	0.031	0.781	-0.052	0.9
MAX	0.920	0.868	3.784	0.138	82.3
COUNT	67	67	67	67	67

(a) one 24-hour sample collected every 12 days
(b) 24-hour average of concentrations measured every 15 minutes

Table 5.1 Average PAN and PCE concentrations for each day of the week in 2002 and their ratios to those measured on Sunday.

	Average concentration, ppbv		Concentration ratio, day of the week/Sunday	
Day of the week	**PAN**	**PCE**	**PAN**	**PCE**
Monday	0.73	0.13	1.21	0.76
Tuesday	0.70	0.18	1.25	0.57
Wednesday	0.76	0.18	1.16	0.55
Thursday	0.78	0.18	1.12	0.54
Friday	0.77	0.16	1.15	0.61
Saturday	0.84	0.14	1.04	0.70
Sunday	0.88	0.10	1.00	1.00

Table 6.1. Linear regression parameters for PPN vs. PAN and for PAN vs. PPN, Azusa, February 2001-September 2003

	Linear Regression PPN vs. PAN, ppbv							Linear Regression PAN vs. PPN, ppbv						
Month-year	m	sm	b	sb	R	R^2	b/AVE, %	m	sm	b	sb	R	R^2	b/AVE, %
F-01	0.067	0.0015	0.003	0.0001	0.868	0.754	38.0	11.32	0.259	-0.017	0.002	0.868	0.754	-21.6
M-01	0.108	0.0002	-0.007	0.0002	0.996	0.991	-9.2	9.19	0.016	0.068	0.002	0.996	0.991	9.2
A-01	0.112	0.0002	-0.005	0.0002	0.997	0.994	-6.1	8.87	0.012	0.048	0.001	0.997	0.994	6.3
M-01	0.118	0.0002	-0.011	0.0003	0.995	0.991	-8.8	8.41	0.016	0.107	0.003	0.995	0.991	9.0
J-01	0.118	0.0002	-0.010	0.0003	0.995	0.990	-9.5	8.38	0.016	0.096	0.002	0.995	0.990	9.6
J-01	0.120	0.0002	-0.007	0.0003	0.995	0.989	-6.4	8.25	0.016	0.071	0.002	0.995	0.989	7.0
A-01	0.123	0.0002	-0.009	0.0004	0.994	0.989	-7.0	8.03	0.016	0.085	0.003	0.994	0.989	7.6
S-01	0.122	0.0003	-0.004	0.0003	0.994	0.988	-3.4	8.07	0.017	0.044	0.003	0.994	0.988	4.5
O-01	0.128	0.0003	-0.006	0.0004	0.991	0.981	-5.2	7.67	0.020	0.069	0.003	0.991	0.981	6.7
N-01	0.122	0.0003	-0.002	0.0002	0.994	0.988	-2.1	8.10	0.017	0.020	0.002	0.994	0.988	3.2
D-01	0.116	0.0005	-0.002	0.0002	0.978	0.956	-5.0	8.22	0.033	0.028	0.001	0.978	0.956	9.0
J-02	0.122	0.0003	-0.001	0.0002	0.989	0.978	-1.0	7.99	0.022	0.014	0.001	0.989	0.978	3.2
F-02	0.131	0.0003	-0.004	0.0002	0.994	0.987	-5.0	7.53	0.017	0.038	0.002	0.994	0.987	5.9
M-02	0.117	0.0003	-0.002	0.0002	0.990	0.981	-2.4	8.42	0.022	0.024	0.002	0.990	0.981	4.2
A-02	0.116	0.0002	-0.007	0.0002	0.995	0.989	-9.1	8.51	0.017	0.070	0.002	0.995	0.989	9.4
M-02	0.124	0.0003	-0.010	0.0003	0.993	0.987	-10.2	7.97	0.017	0.095	0.002	0.993	0.987	10.5
J-02	0.128	0.0002	-0.011	0.0003	0.995	0.990	-9.0	7.72	0.015	0.097	0.002	0.995	0.990	9.2
J-02	0.129	0.0002	-0.009	0.0003	0.995	0.990	-8.2	7.70	0.014	0.080	0.002	0.995	0.990	8.5
A-02	0.127	0.0004	-0.007	0.0006	0.984	0.968	-5.3	7.62	0.025	0.094	0.004	0.984	0.968	8.1
S-02	0.122	0.0003	-0.003	0.0004	0.992	0.985	-2.5	8.08	0.023	0.035	0.003	0.992	0.985	3.9
O-02	0.125	0.0004	-0.012	0.0005	0.989	0.978	-9.2	7.84	0.023	0.117	0.003	0.989	0.978	10.5
N-02	0.124	0.0002	-0.003	0.0002	0.994	0.989	-5.4	7.95	0.016	0.032	0.001	0.994	0.989	6.2
D-02	0.121	0.0003	-0.001	0.0002	0.988	0.976	-1.6	8.07	0.023	0.016	0.001	0.988	0.976	3.9
J-03	0.124	0.0005	0.000	0.0002	0.978	0.957	-0.5	7.72	0.030	0.016	0.002	0.978	0.957	4.7
F-03	0.117	0.0003	-0.002	0.0002	0.989	0.979	-3.5	8.37	0.024	0.024	0.001	0.989	0.979	5.4
M-03	0.125	0.0002	-0.004	0.0002	0.996	0.991	-4.4	7.94	0.014	0.034	0.001	0.996	0.991	5.0
A-03	0.113	0.0002	0.000	0.0001	0.994	0.989	-0.7	8.76	0.018	0.009	0.001	0.994	0.989	1.8
M-03	0.128	0.0003	-0.010	0.0004	0.993	0.987	-8.5	7.72	0.016	0.094	0.003	0.993	0.987	9.1
J-03	0.126	0.0002	-0.015	0.0003	0.996	0.991	-12.4	7.84	0.014	0.131	0.002	0.996	0.991	11.8
J-03	0.122	0.0002	-0.004	0.0003	0.995	0.991	-3.0	8.12	0.015	0.041	0.003	0.995	0.991	3.9
A-03	0.123	0.0003	-0.005	0.0003	0.992	0.985	-5.3	8.00	0.018	0.052	0.002	0.992	0.985	6.5
S-03	0.119	0.0005	-0.004	0.0007	0.984	0.969	-2.8	8.14	0.031	0.063	0.005	0.984	0.969	5.8
AVE (a)	0.122	0.0003	-0.006	0.0003	0.992	0.984	-5.6	8.10	0.019	0.058	0.002	0.992	0.984	6.8
MIN	0.108	0.0002	-0.015	0.0001	0.978	0.956	-12.4	7.53	0.012	0.009	0.001	0.978	0.956	1.8
MAX	0.131	0.0005	0.000	0.0007	0.997	0.994	-0.5	9.19	0.033	0.131	0.005	0.997	0.994	11.8
RANGE	0.023		0.015				11.9	1.66		0.122				10.0
Year														
2001	0.119	0.0001	-0.006	0.0001	0.992	0.984	-6.1	8.27	0.006	0.062	0.001	0.992	0.984	7.2
2002	0.124	0.0001	-0.005	0.0001	0.991	0.983	-5.8	7.94	0.006	0.055	0.001	0.991	0.983	7.1
2003	0.122	0.0001	-0.005	0.0001	0.993	0.986	-5.0	8.06	0.006	0.048	0.001	0.993	0.986	3.9

(a)February 2001 not included

Table 7.1 Ambient PAN and PPN in Azusa between 1987 and 2003

Year	PAN, ppb			PPN, ppb		
	highest concentration	highest 24-hour average	highest monthly average	highest concentration	highest 24-hour average	highest monthly average
1987 (a)	13	4.8	-	-	-	-
1993 (b)	6.1	3.0	-	1.46	0.88	-
1997 (c)	4.8	2.1	0.98	0.72	-	-
2001 (d)	7.4	2.21	1.20	0.97	0.25	0.13
2002 (d)	6.4	1.96	1.16	0.83	0.25	0.14
2003 (d)	6.5	2.45	1.11	0.86	0.31	0.13

(a) June 19, 24 and 25, July 13 - 15, August 27 - 31 and September 1 - 3, as part of SCAQS (Williams and Grosjean, 1990).

(b) August 28 - September 13 (Grosjean, et al., 1996).

(c) July 14 - October 16, as part of SCOS97-NARSTO (Grosjean, et al., 2001). PPN was measured only on 17 days ("IOP days").

(d) This study, February 2001 - September 2003.

Figure 3.1 Frequency distribution of PAN concentrations, 2003

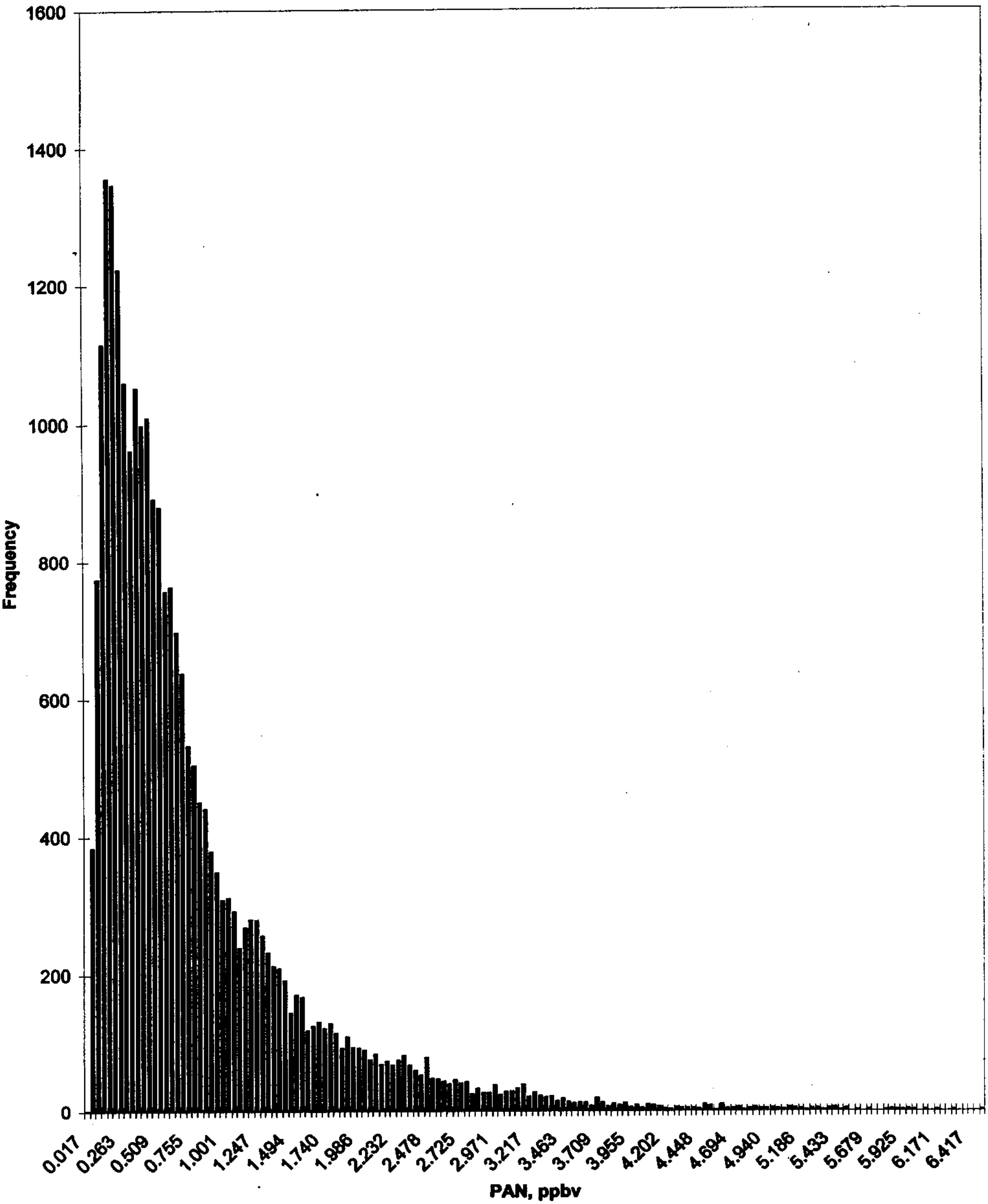

Figure 3.2 Frequency distribution of log PAN, 2003

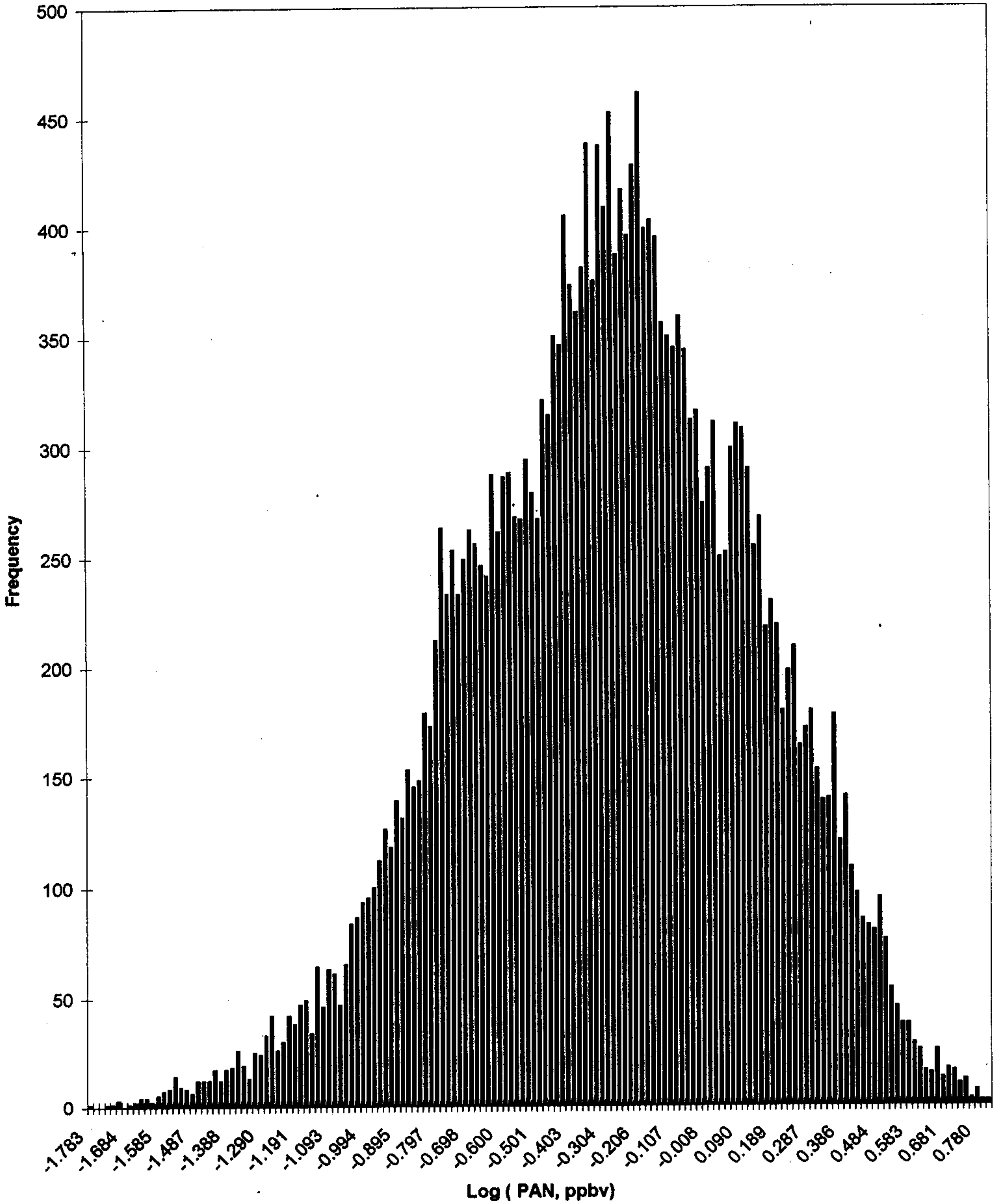

Figure 3.3 Frequency distribution of PCE concentrations, 2003

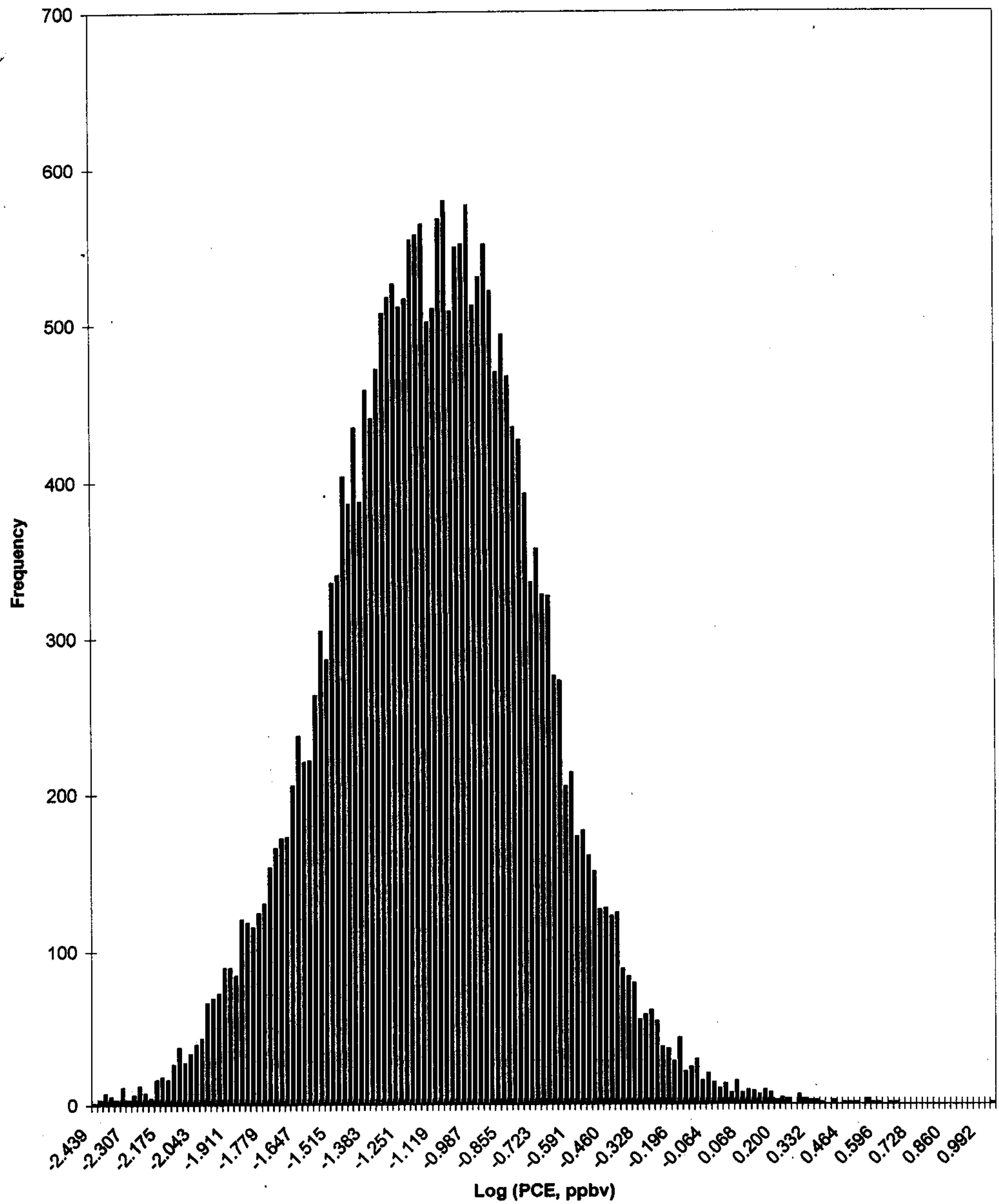

Figure 3.4 Frequency distribution of the PPN/PAN concentration ratio, 2003

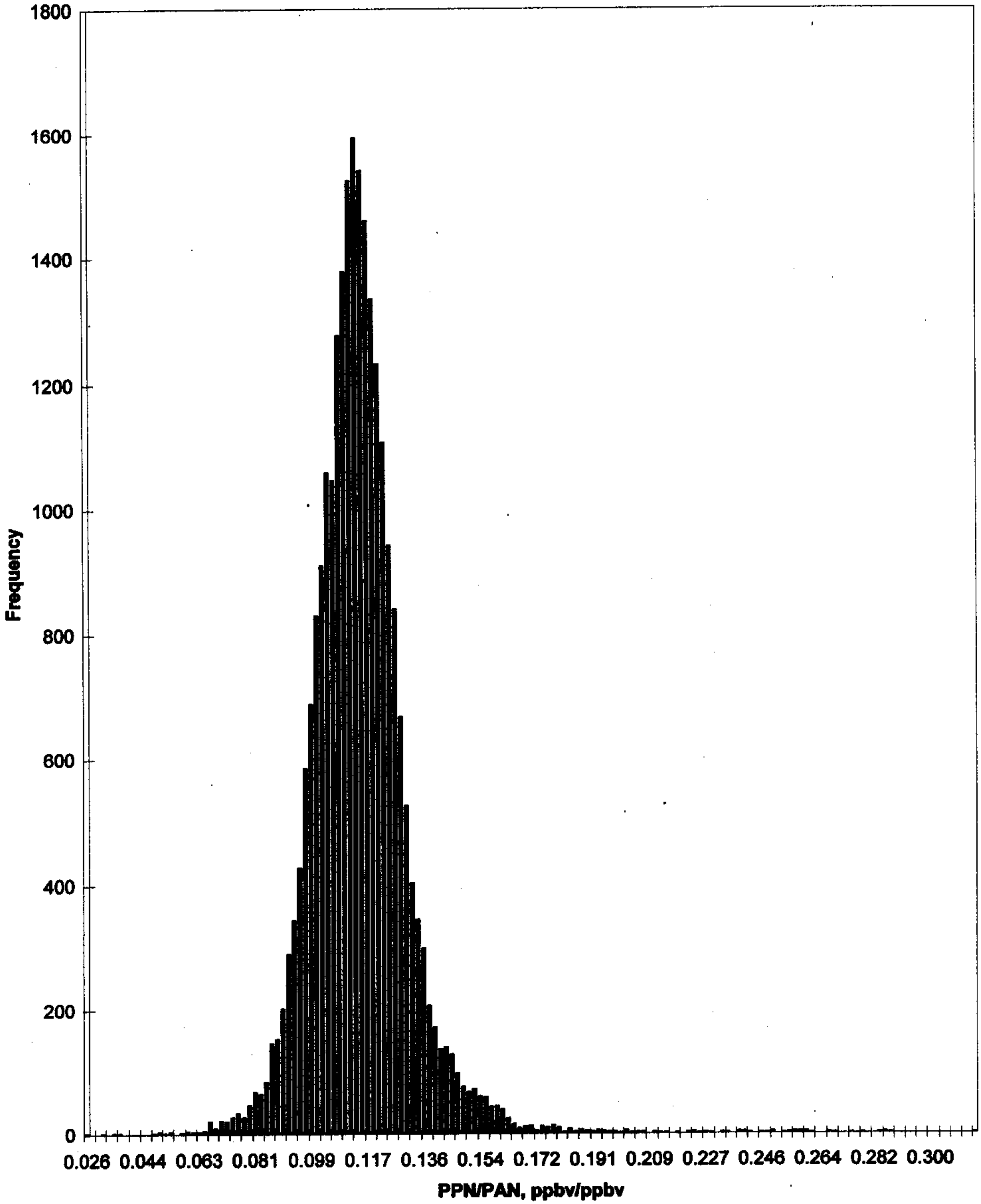

Figure 3.5 Time series plot of ambient PAN concentrations, 2001

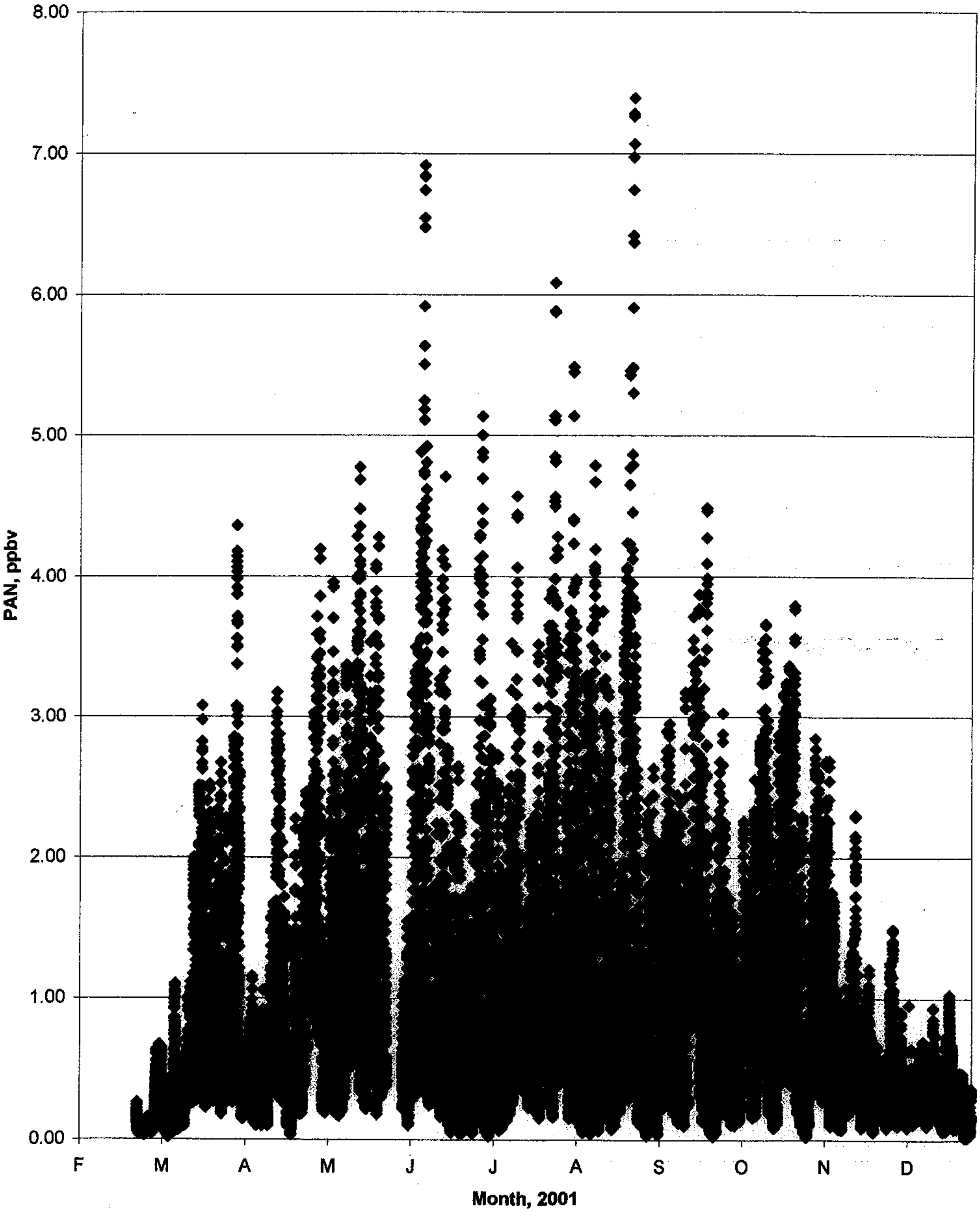

Figure 3.6 Time series plot of ambient PAN concentrations, 2002

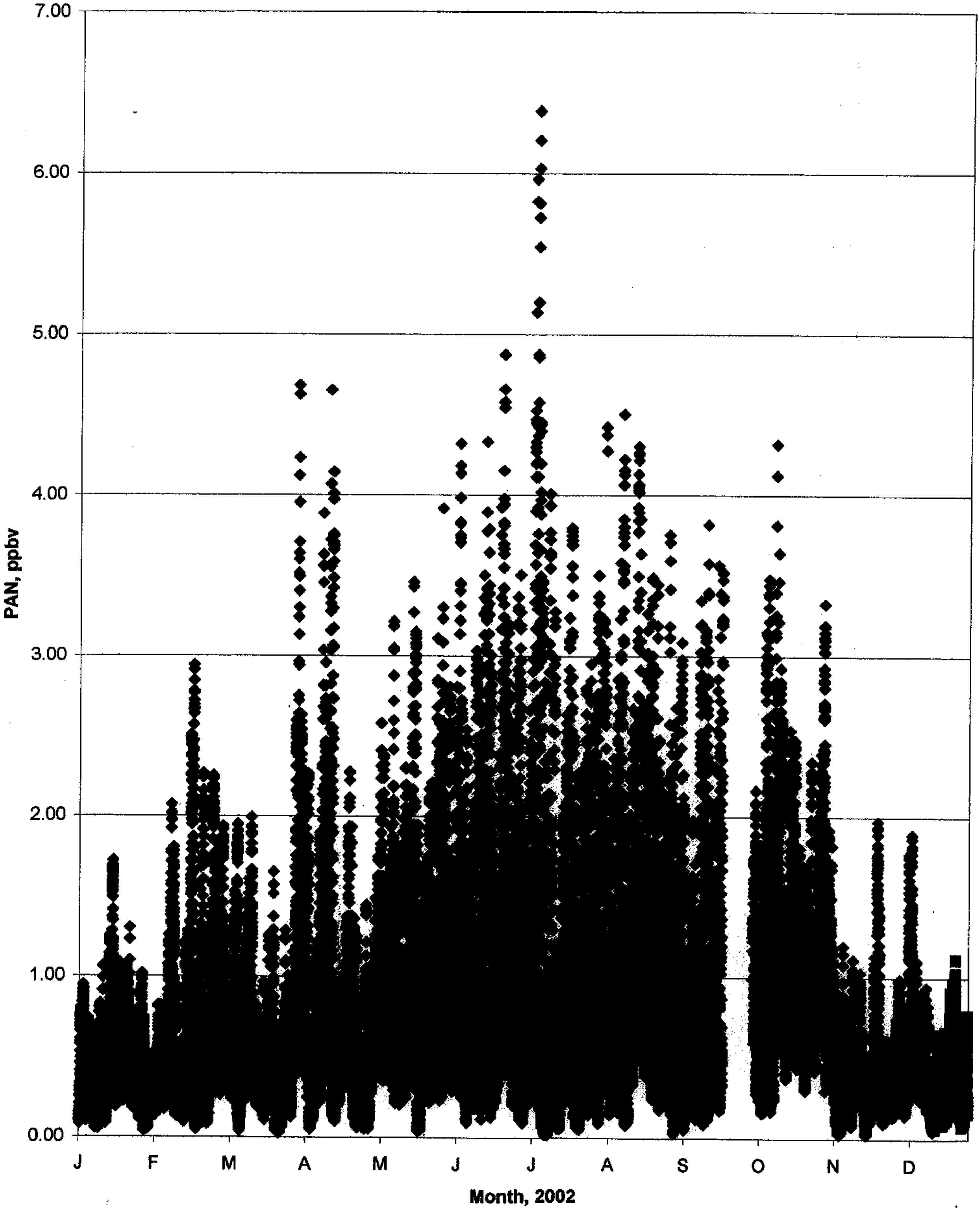

Figure 3.7 Time series plot of ambient PAN concentrations, 2003

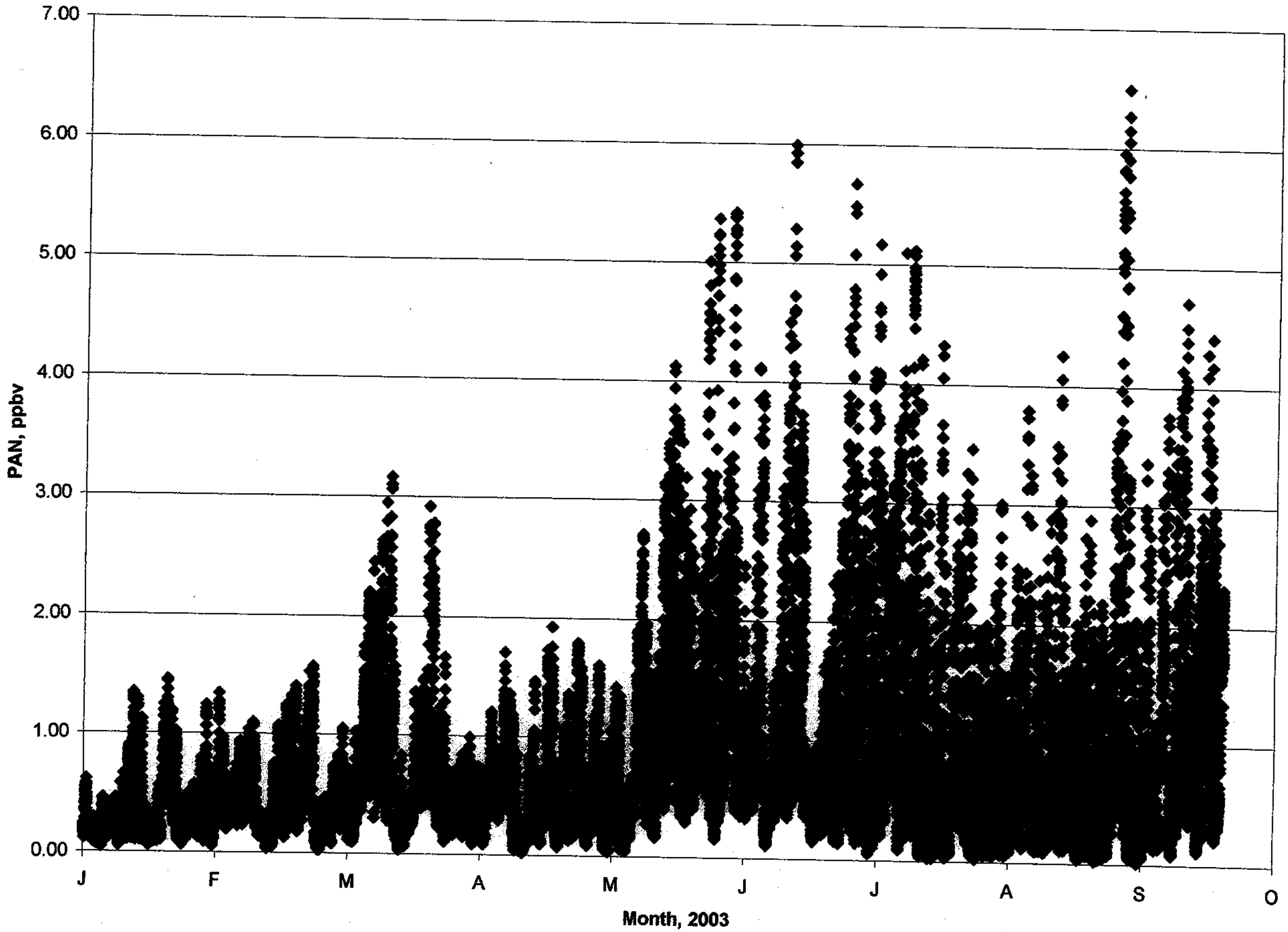

Figure 3.8 Time series plot of ambient PPN concentrations, 2001

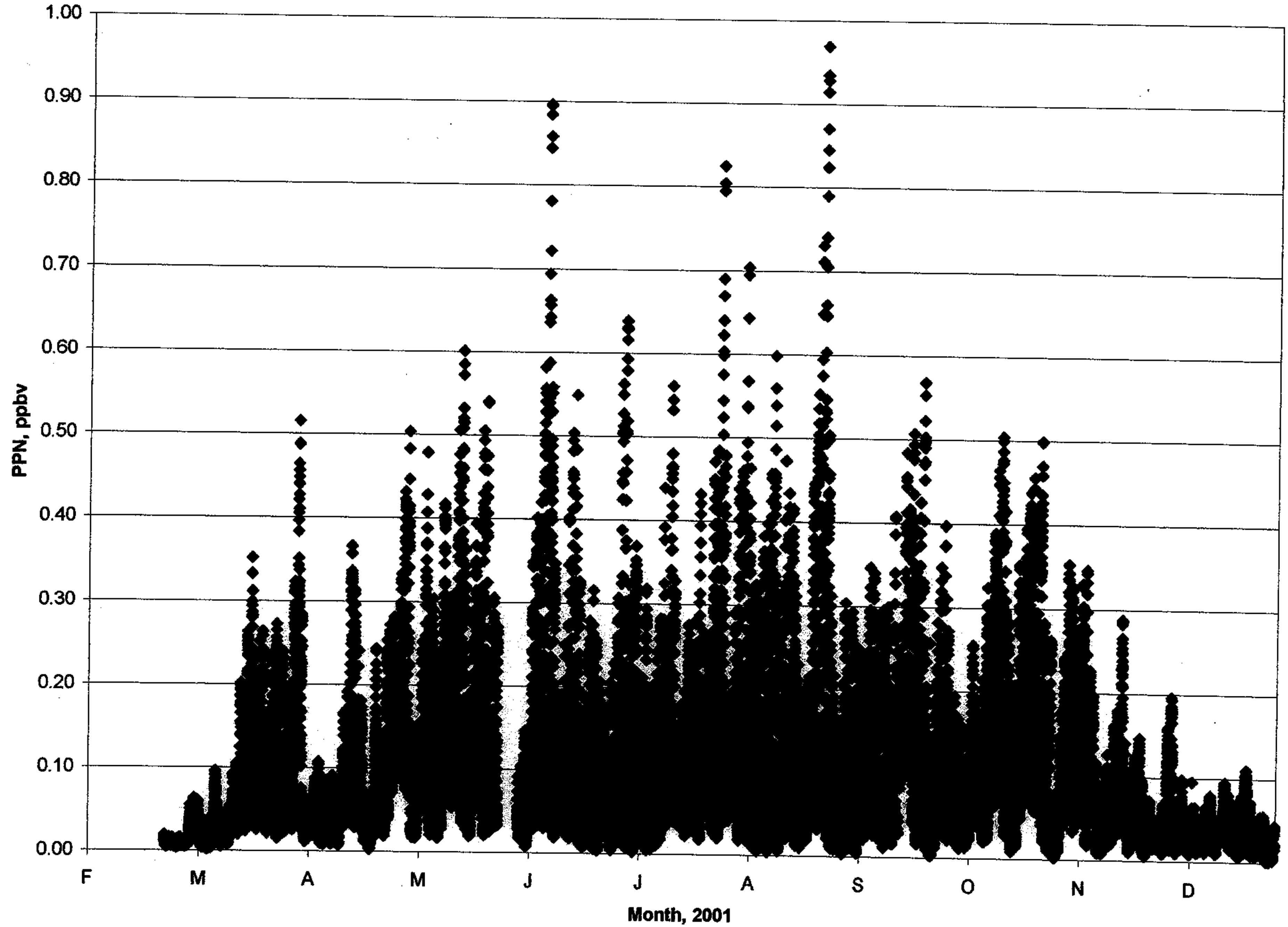

Figure 3.9 Time series plot of ambient PPN concentrations, 2002

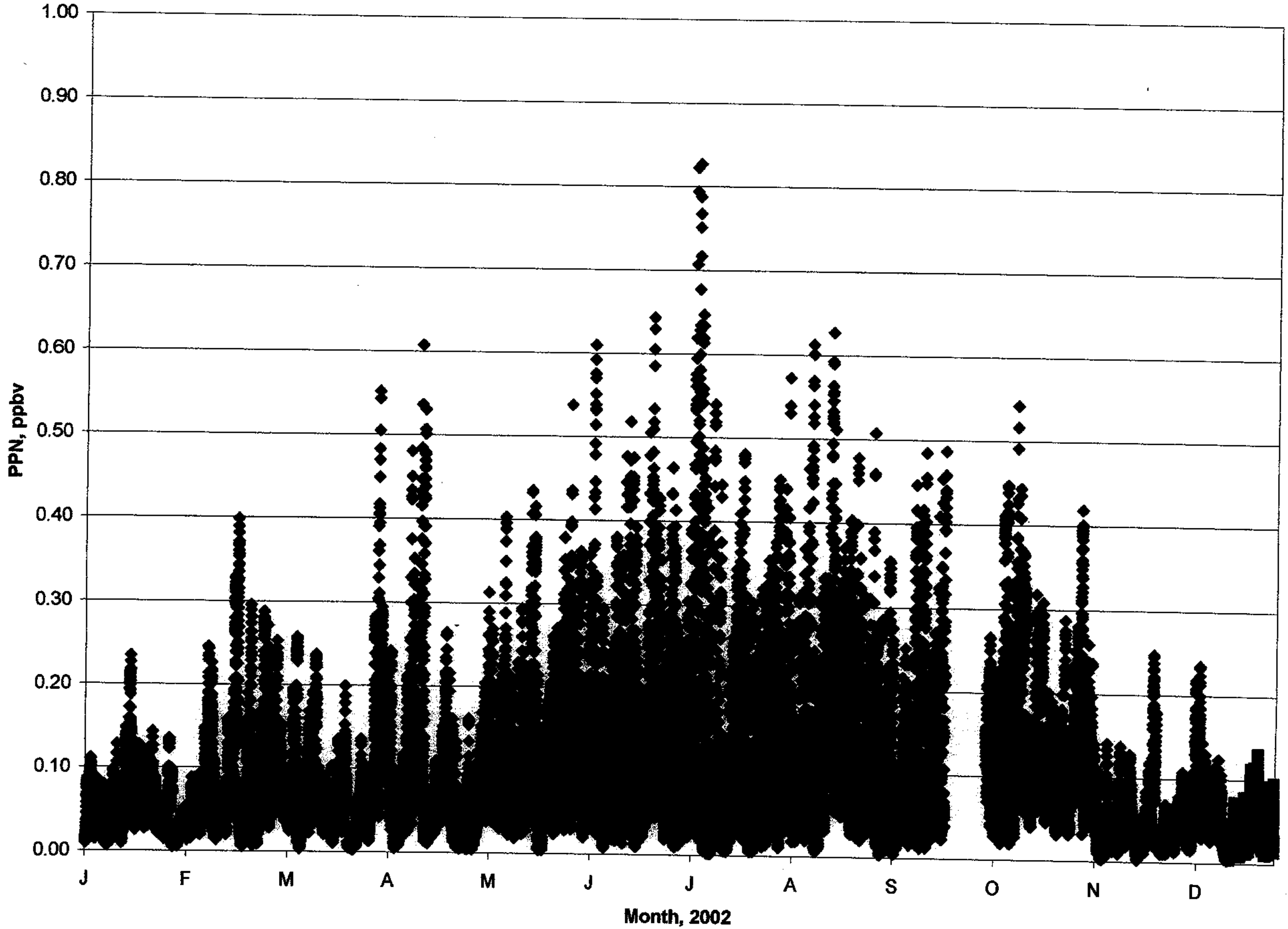

Figure 3.10 Time series plot of ambient PPN concentrations, 2003

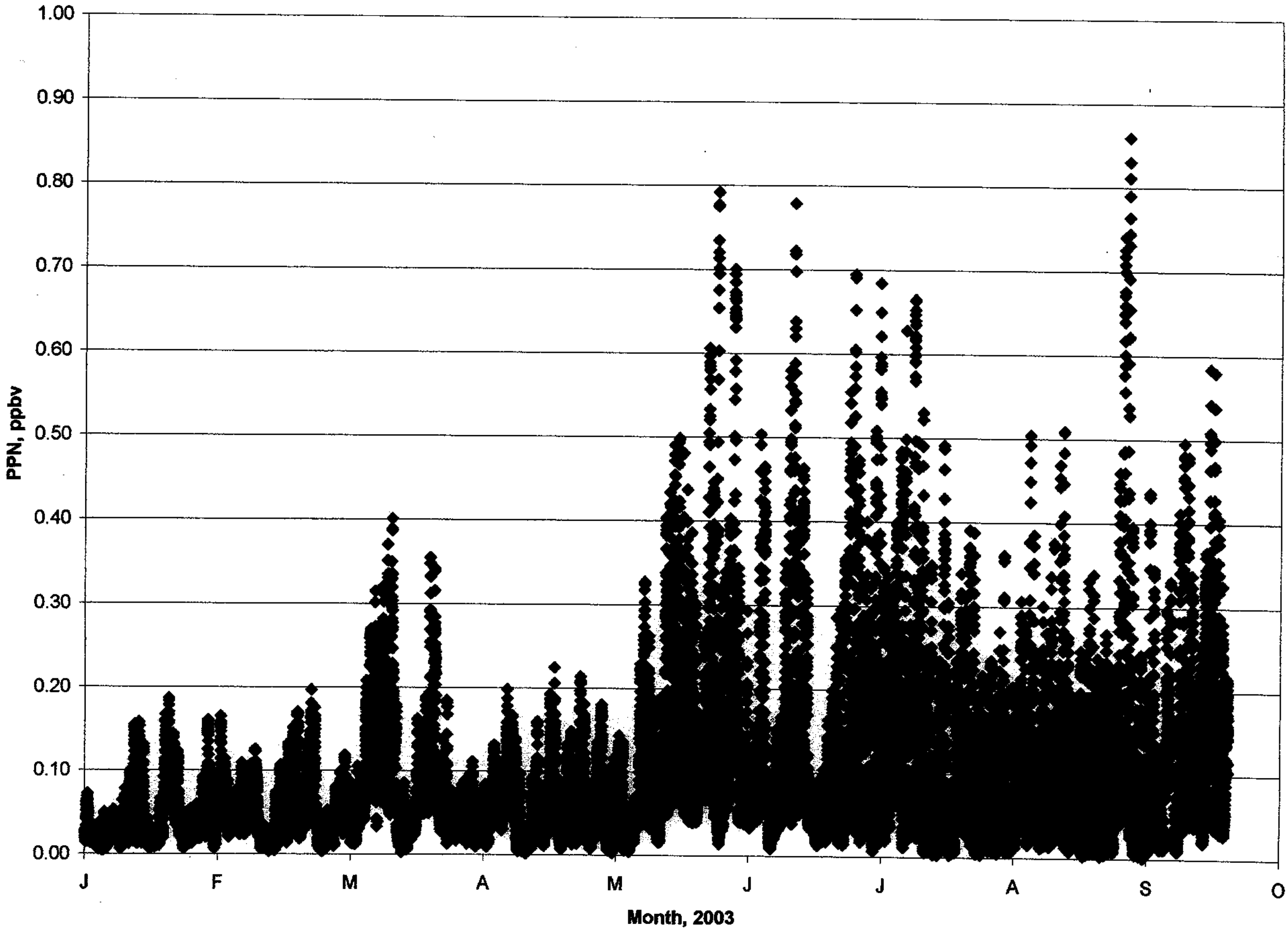

Figure 3.11 Time series plot of ambient PCE concentrations, 2001

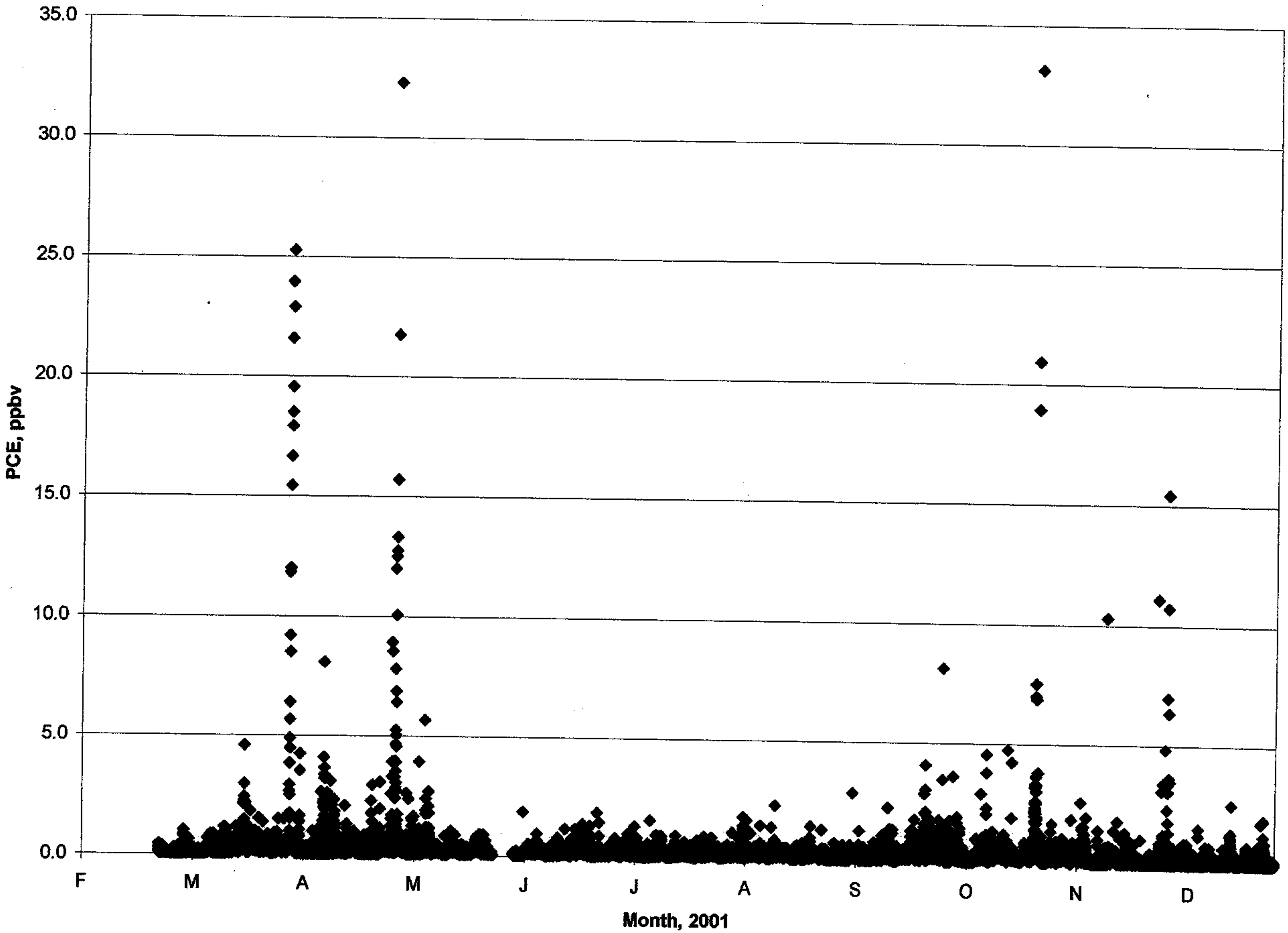

Figure 3.12 Time series plot of ambient PCE concentrations, 2002

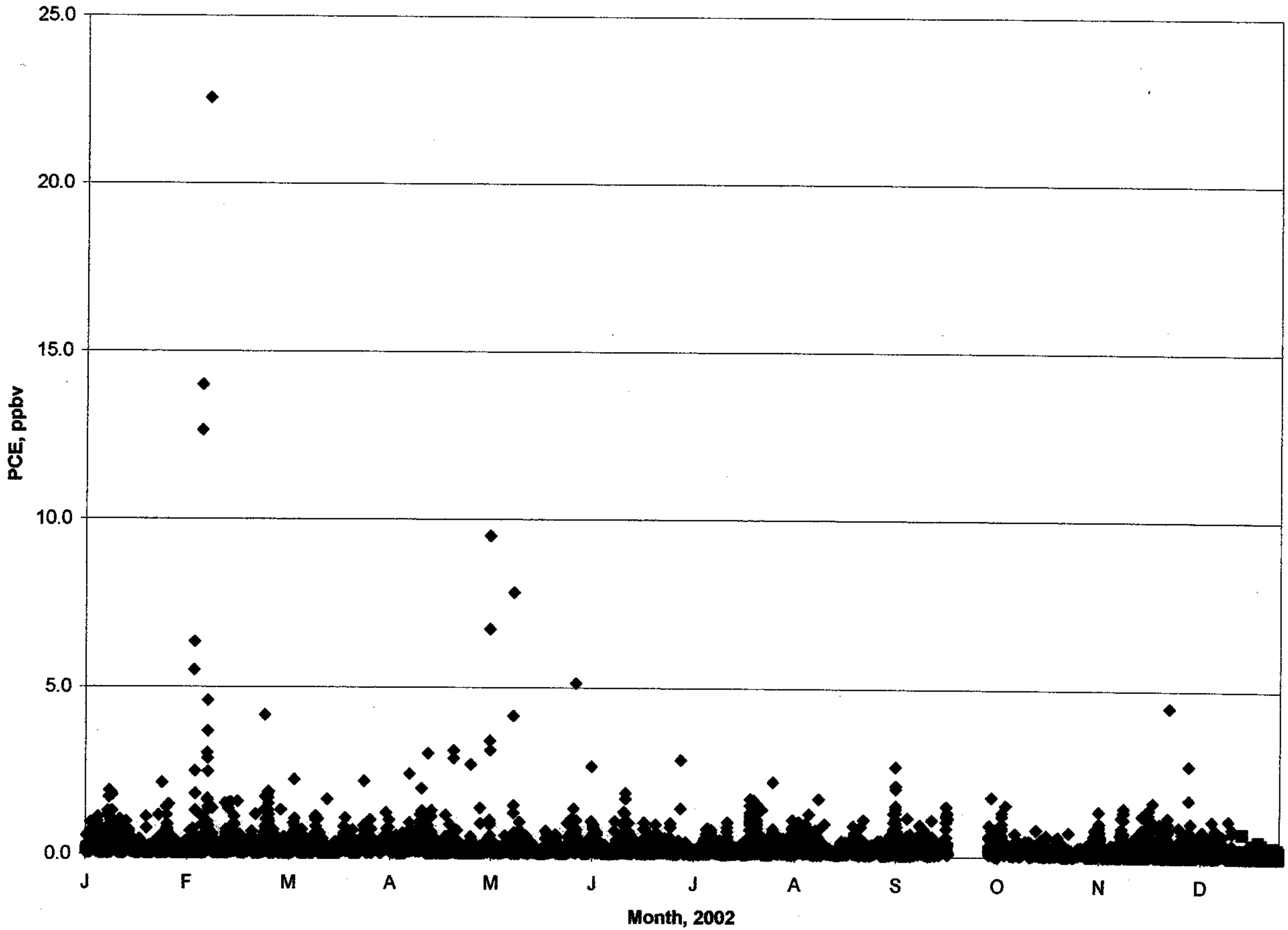

Figure 3.13 Time series plot of ambient PCE concentrations, 2003

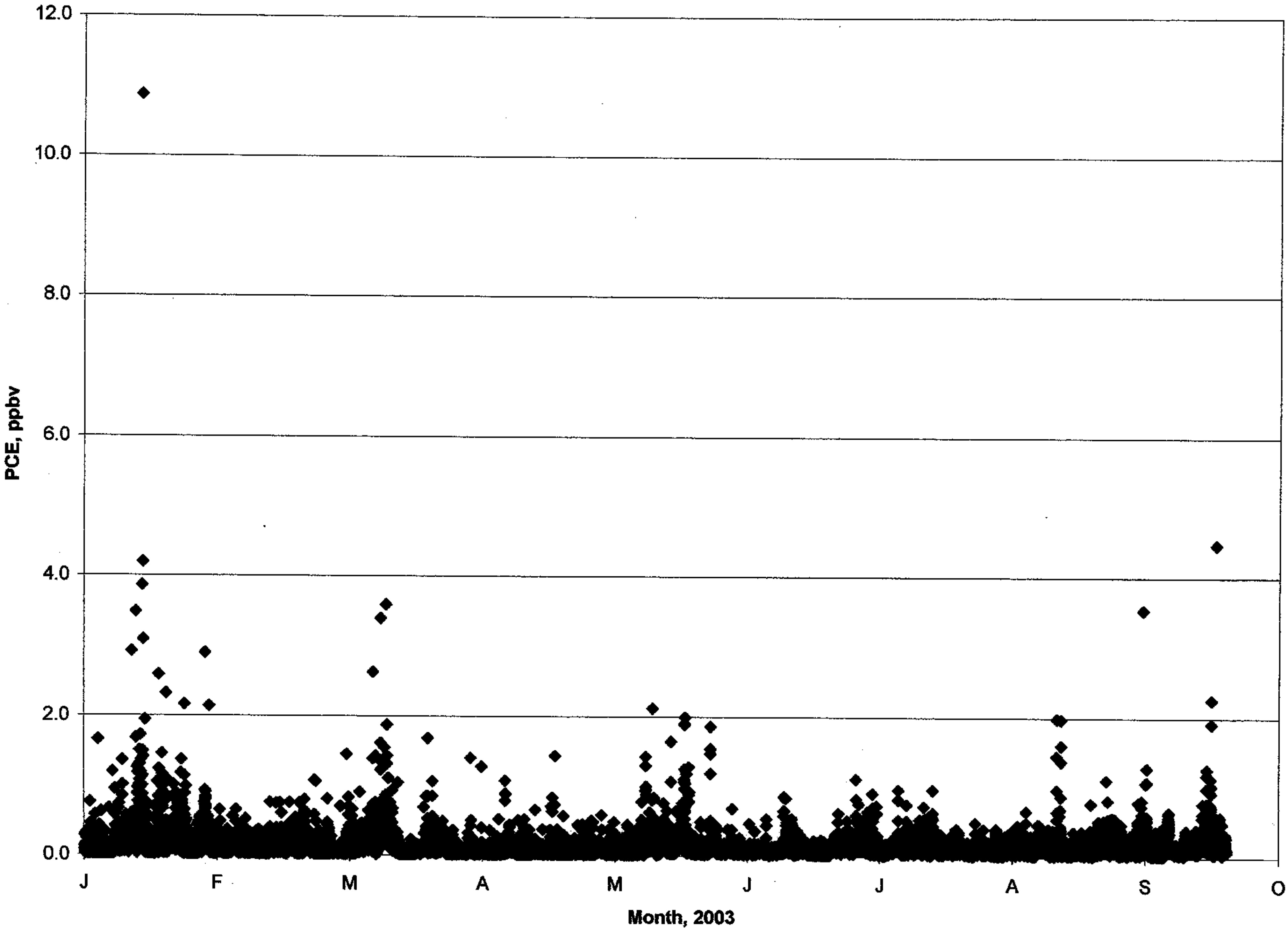

Figure 3.14 Time series plot of PPN/PAN concentration ratio, 2001

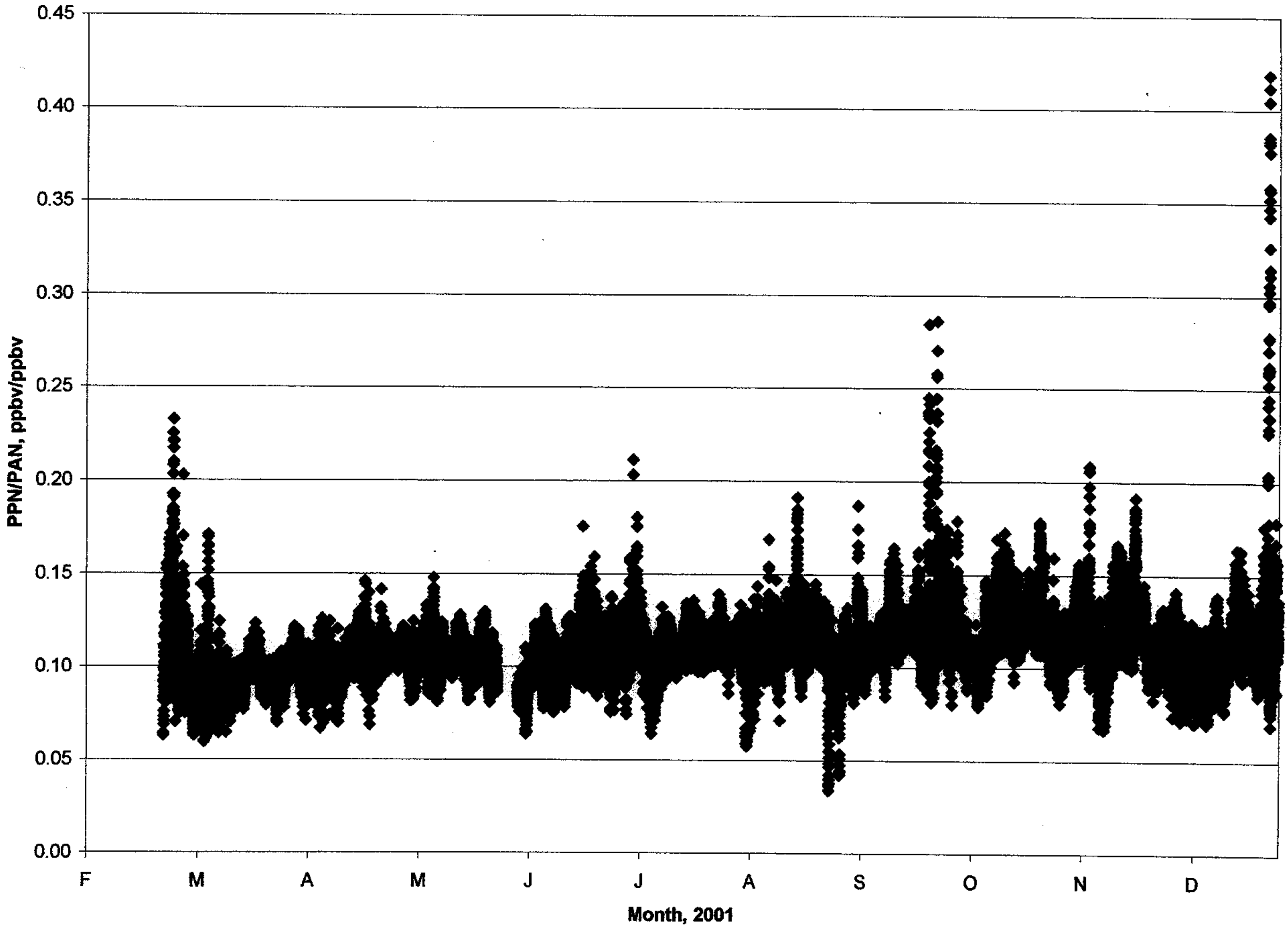

Figure 3.15 Time series plot of PPN/PAN concentration ratio, 2002

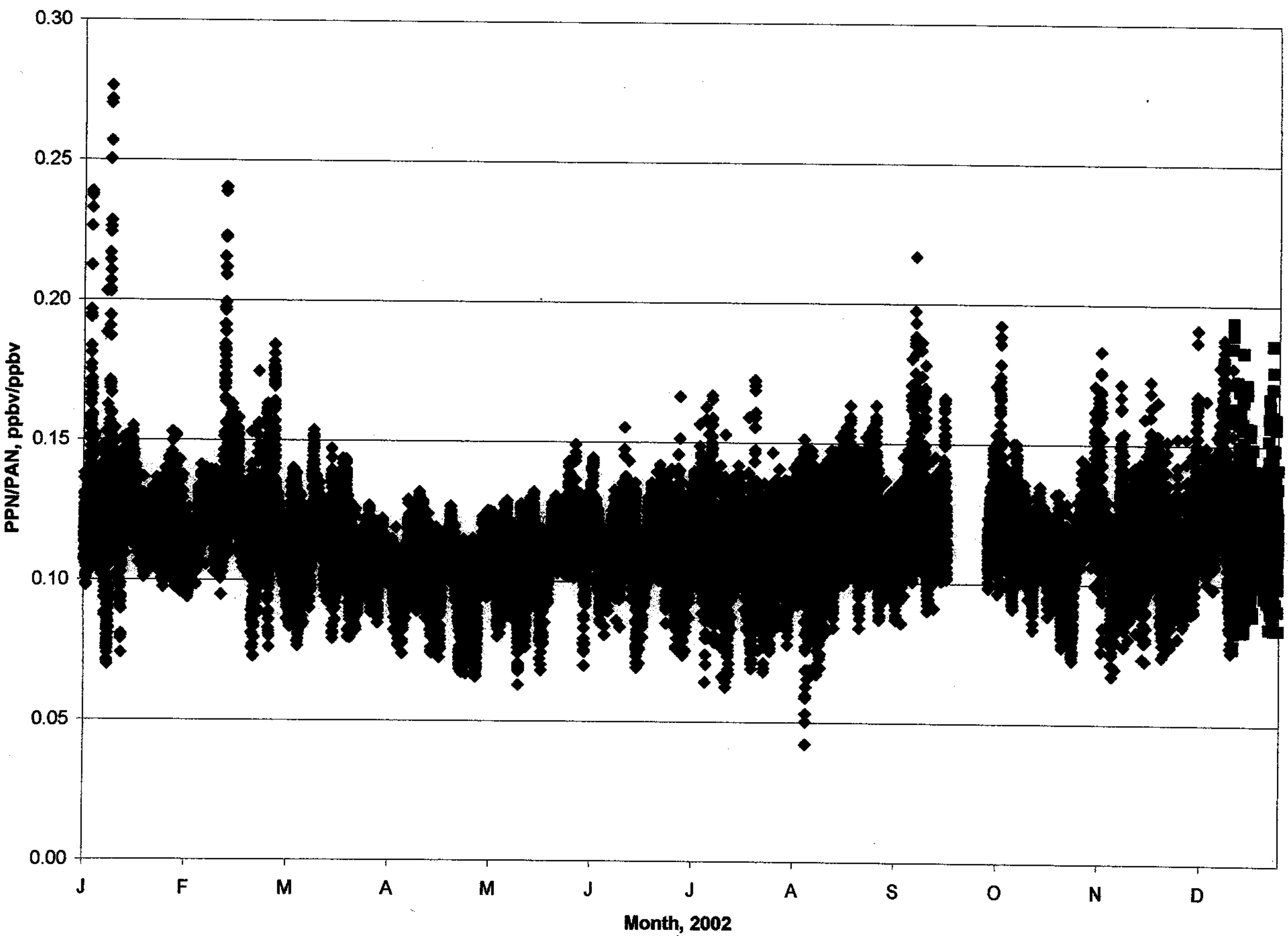

Figure 3.16 Time series plot of PPN/PAN concentration ratio, 2003

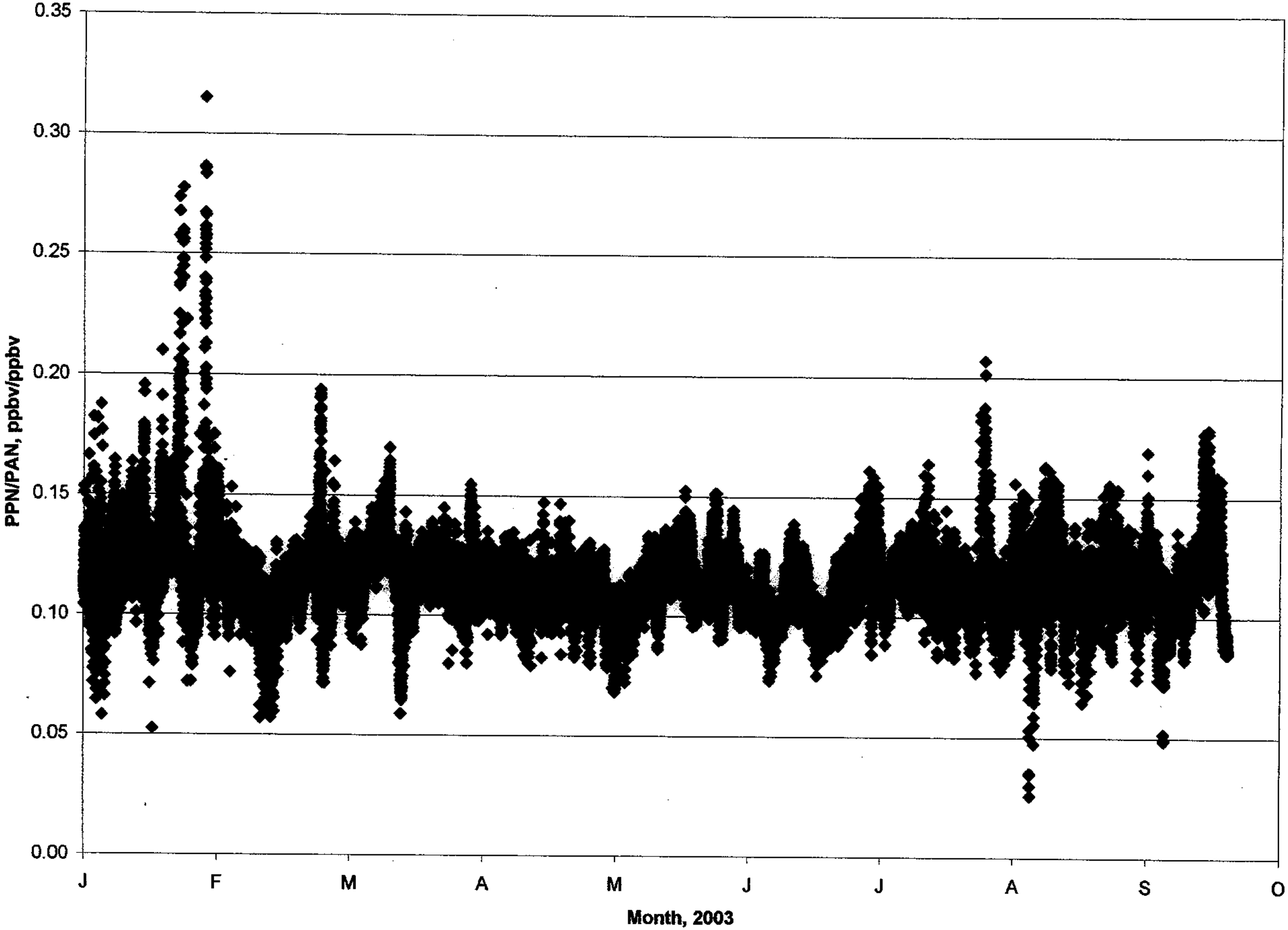

Figure 4.1 Time series plot of monthly averaged PAN and PPN concentrations

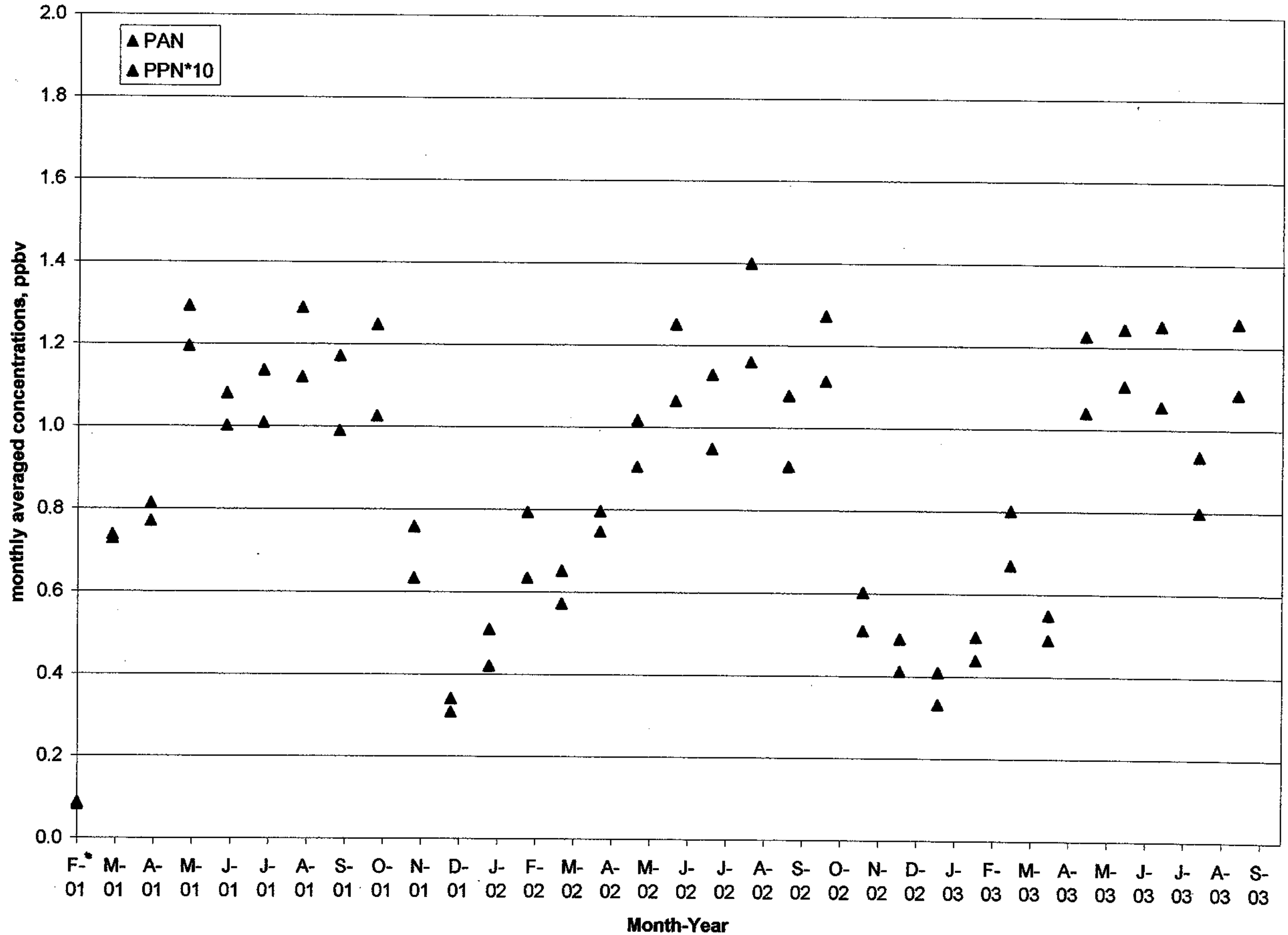

Figure 4.2 Time series plot of maximum PAN concentration calculated from the monthly composite diurnal profiles shown in Figures 4.3, 4.4 and 4.5

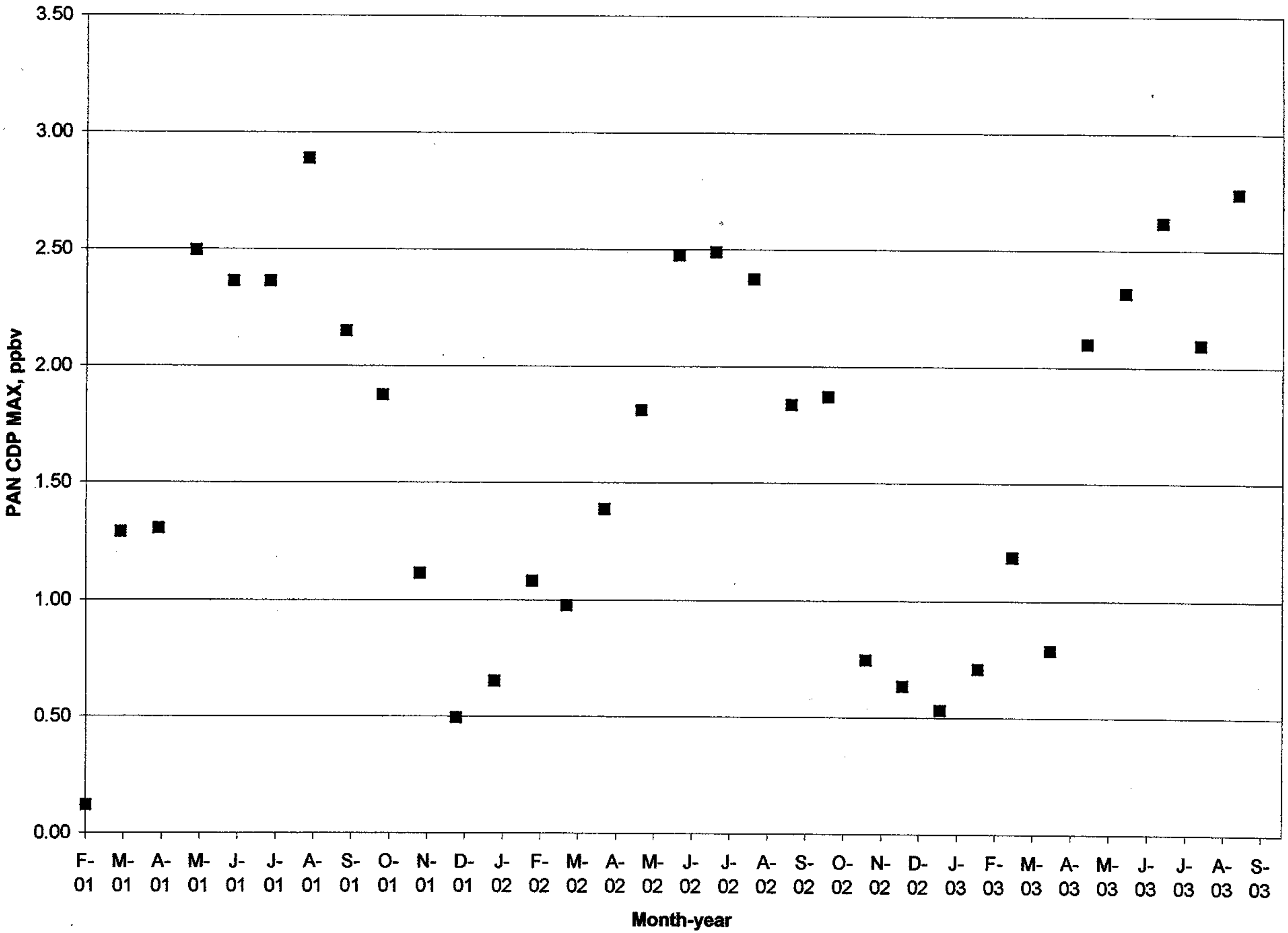

Figure 4.3 Monthly composite diurnal profiles for PAN, 2001

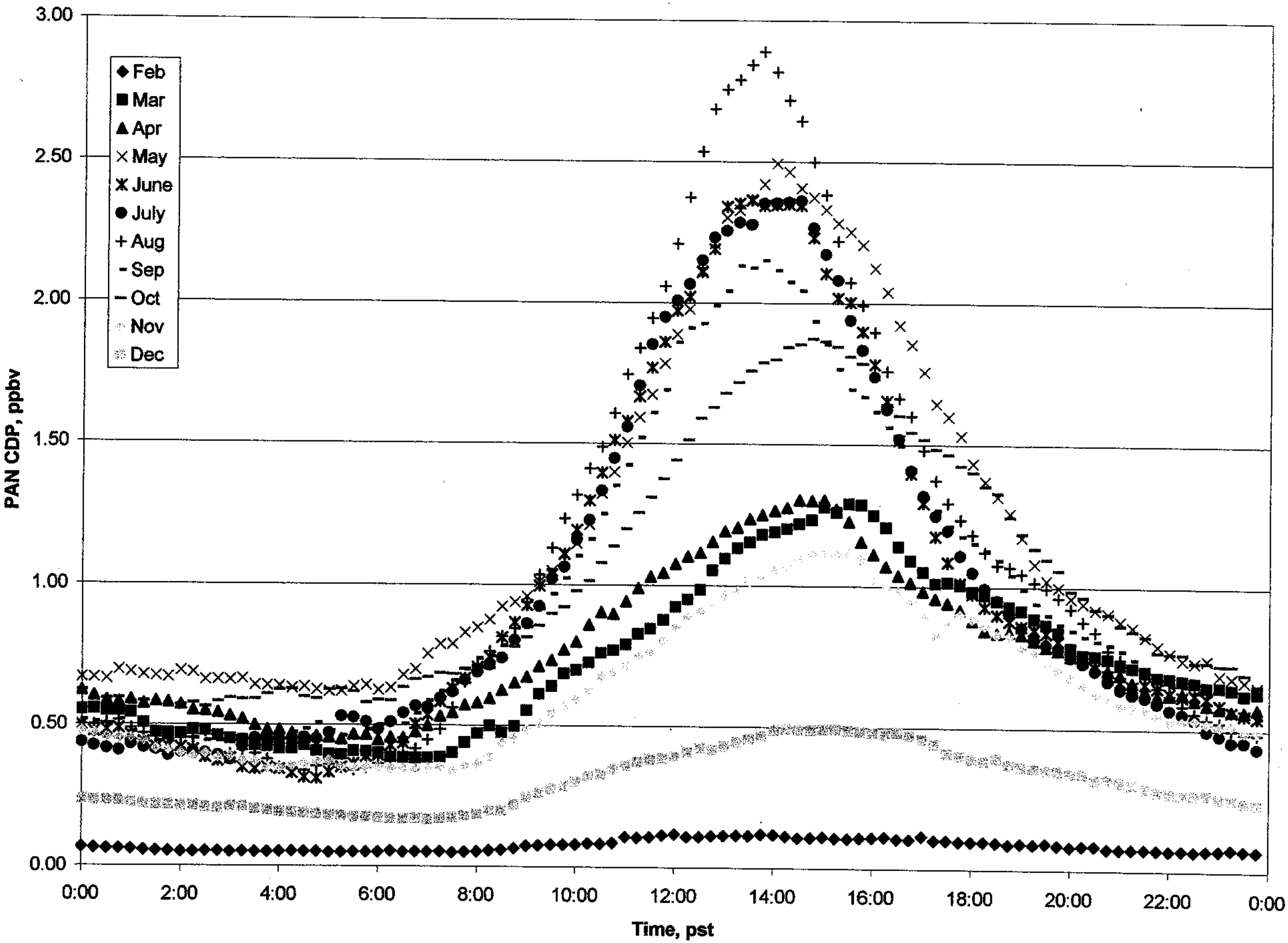

Figure 4.4 Monthly composite diurnal profiles for PAN, 2002

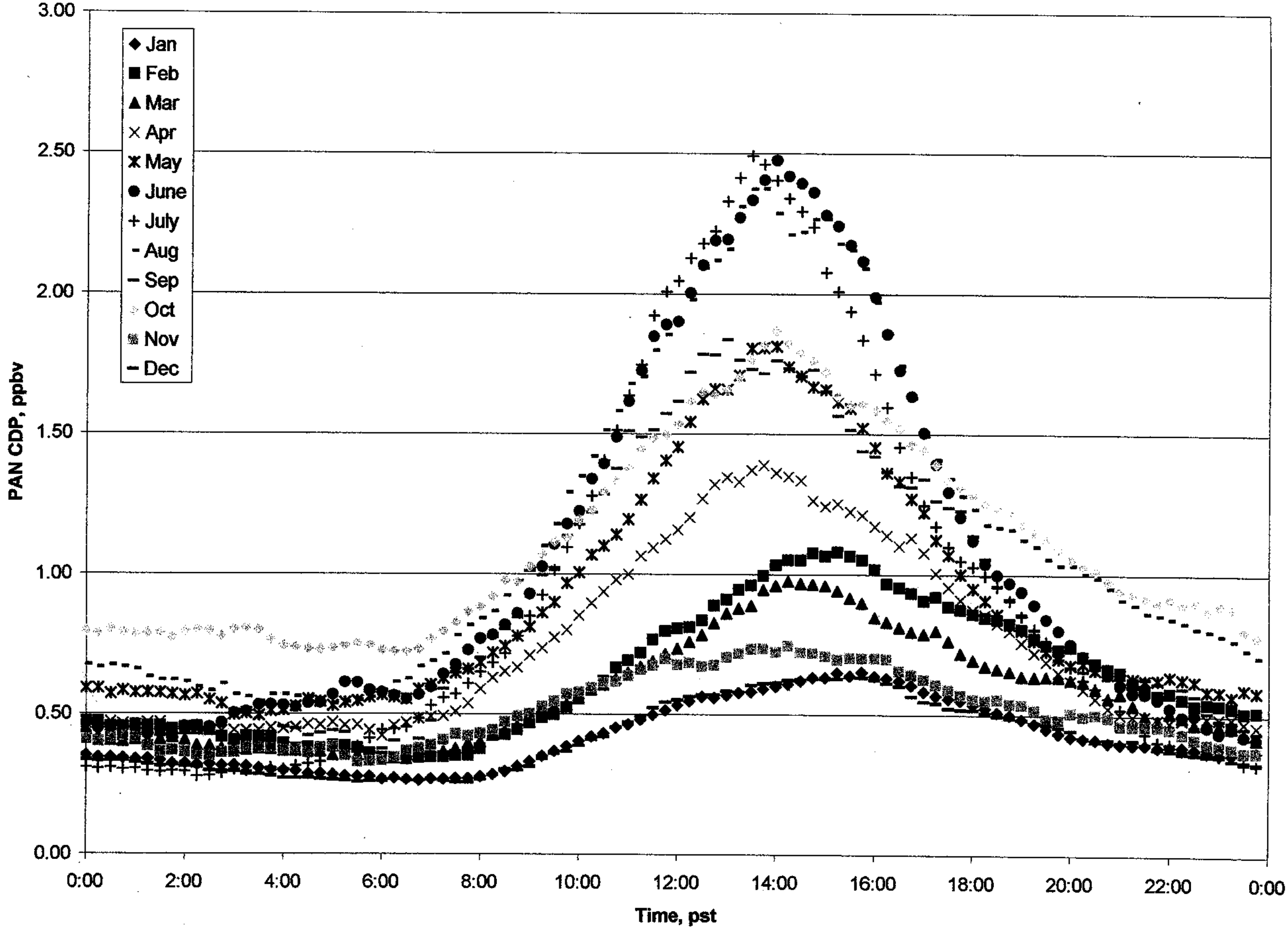

Figure 4.5 Monthly composite diurnal profiles for PAN, 2003

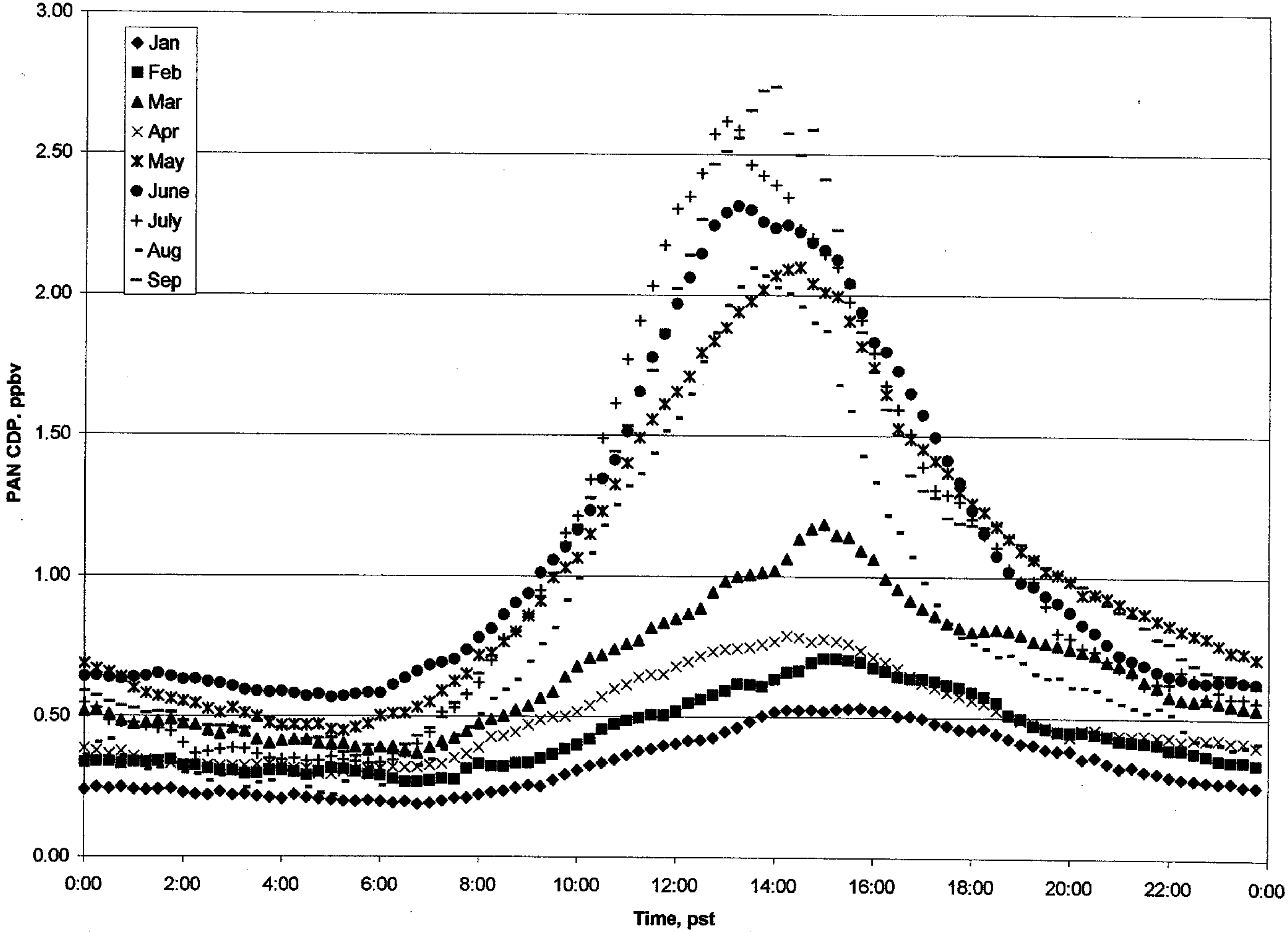

Figure 4.6 Monthly composite diurnal profiles for PPN, 2001

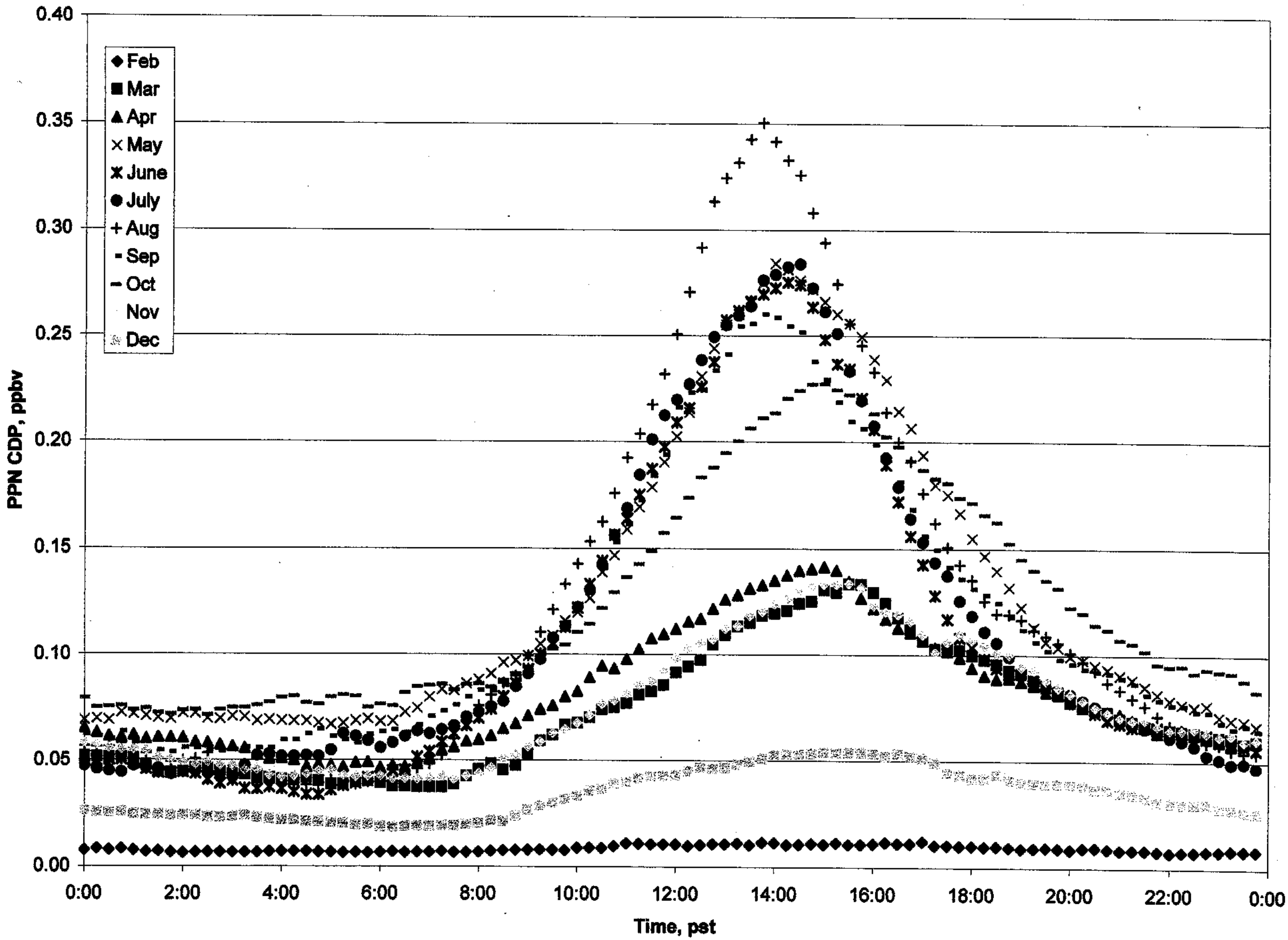

Figure 4.7 Monthly composite diurnal profiles for PPN, 2002

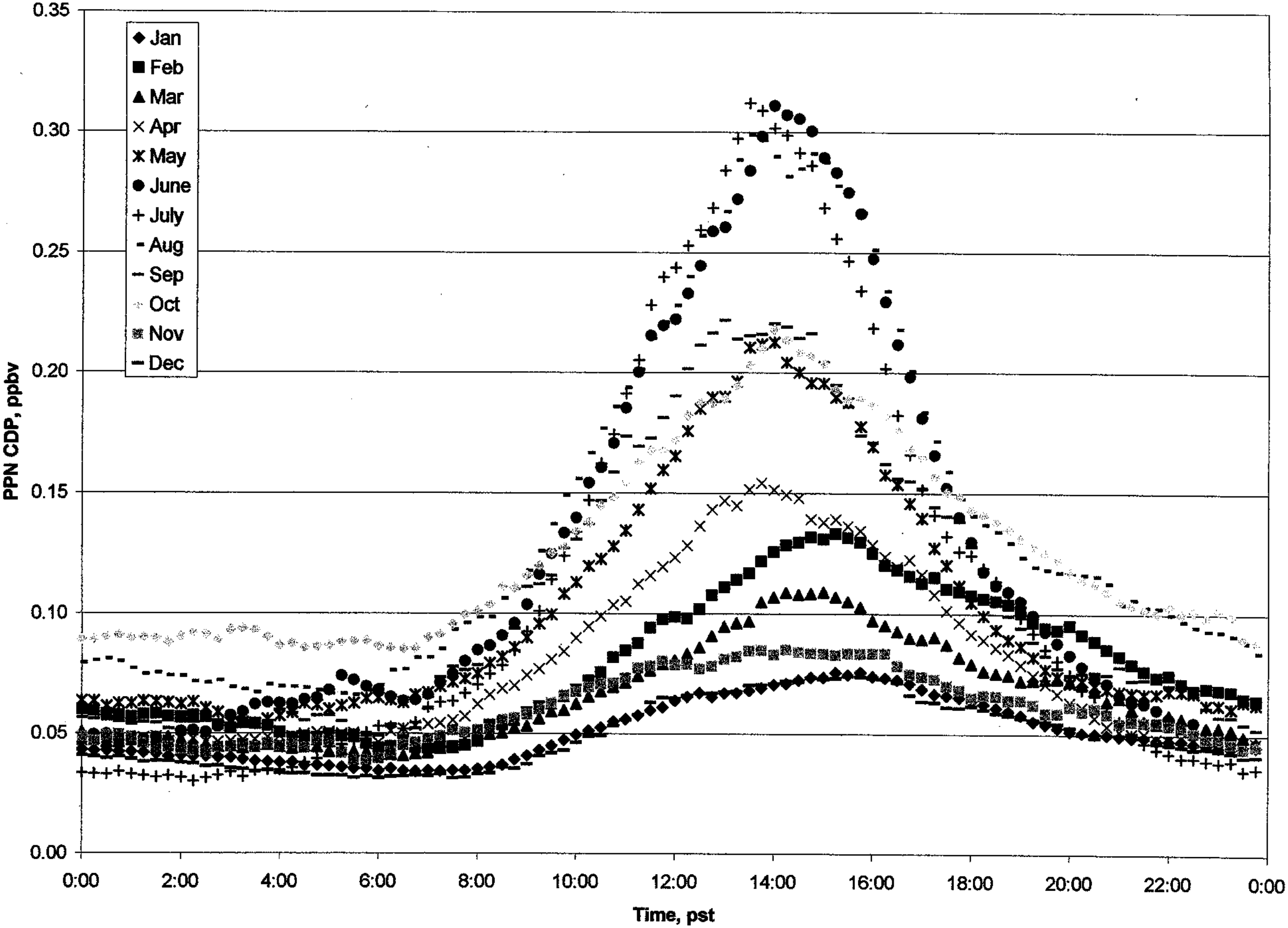

Figure 4.8 Monthly composite diurnal profiles for PPN, 2003

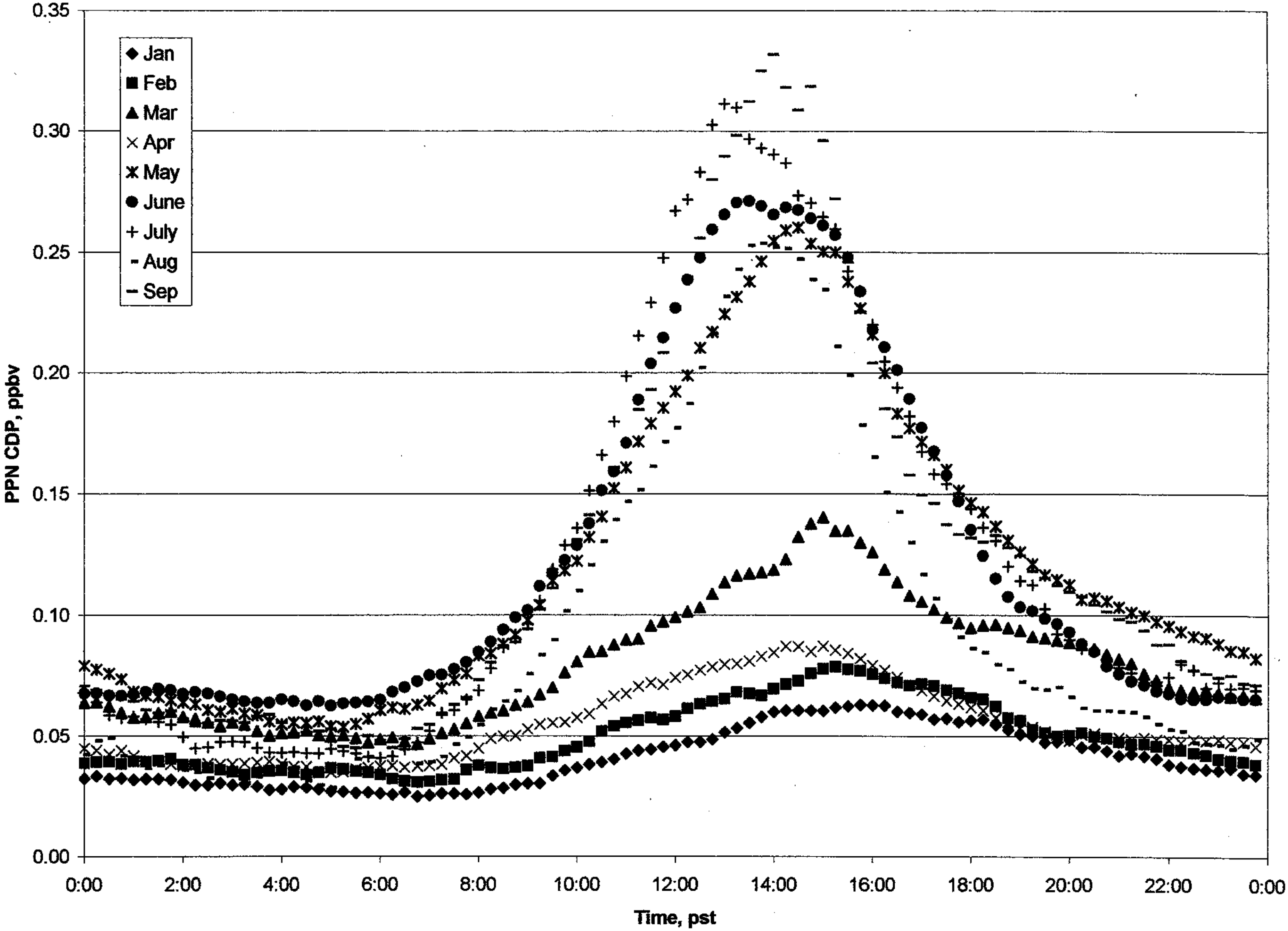

Figure 4.9 Time series plot of monthly averaged PCE concentrations

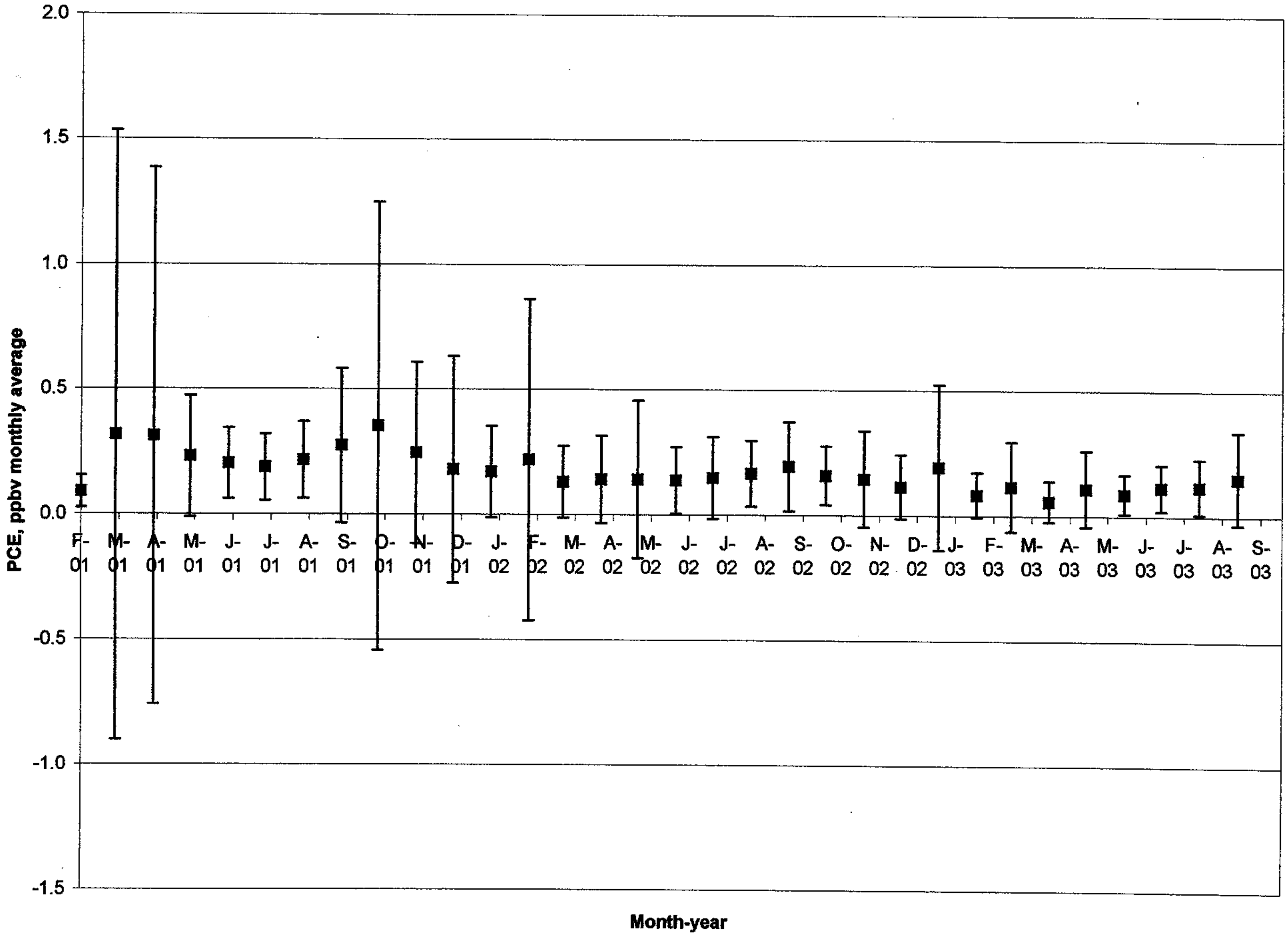

Figure 4.10 Scatterplot of monthly averaged concentrations of PCE vs. those of PAN

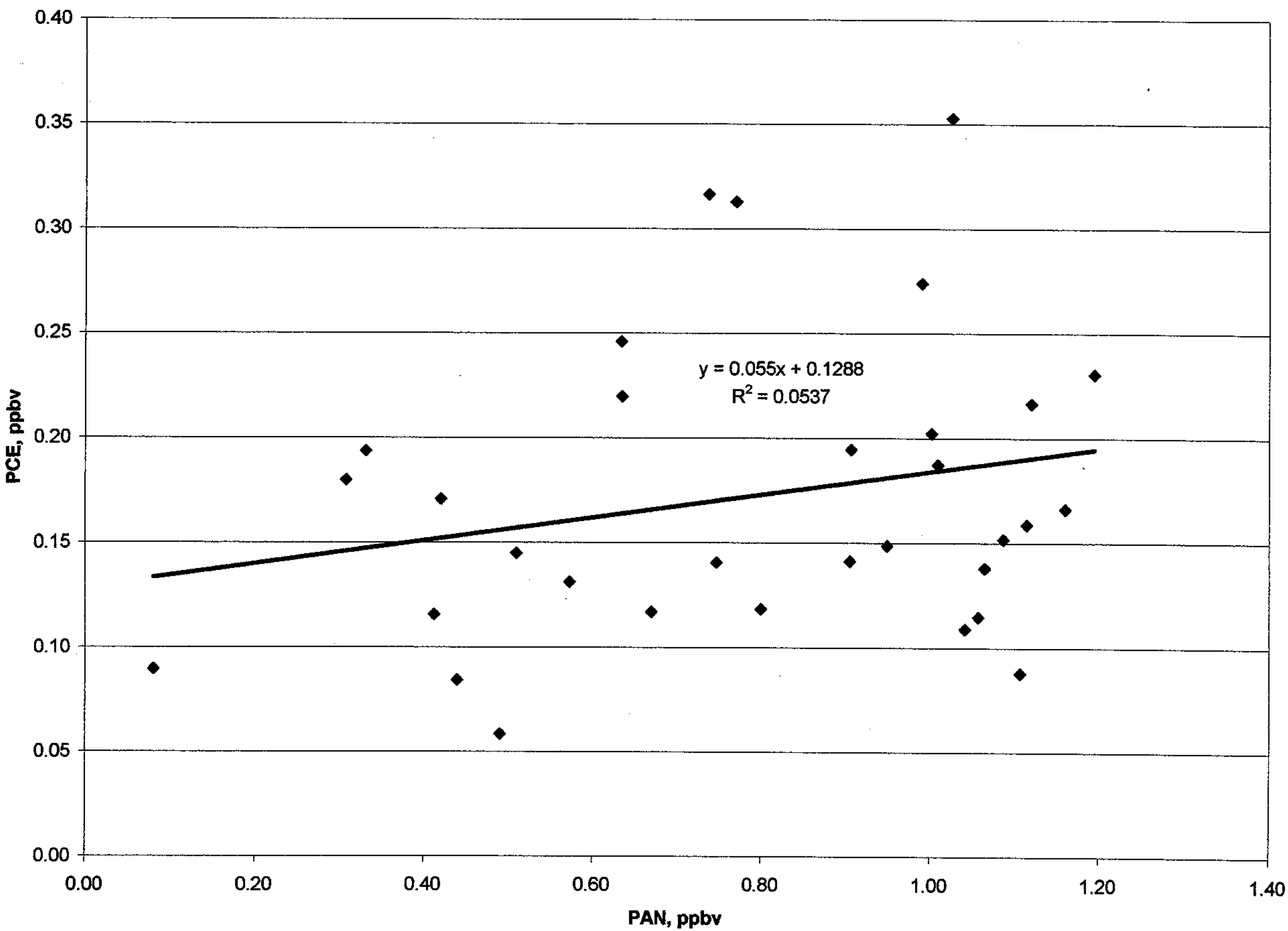

Figure 4.11 Time series plot of the PAN/PCE ratio of monthly averaged concentrations

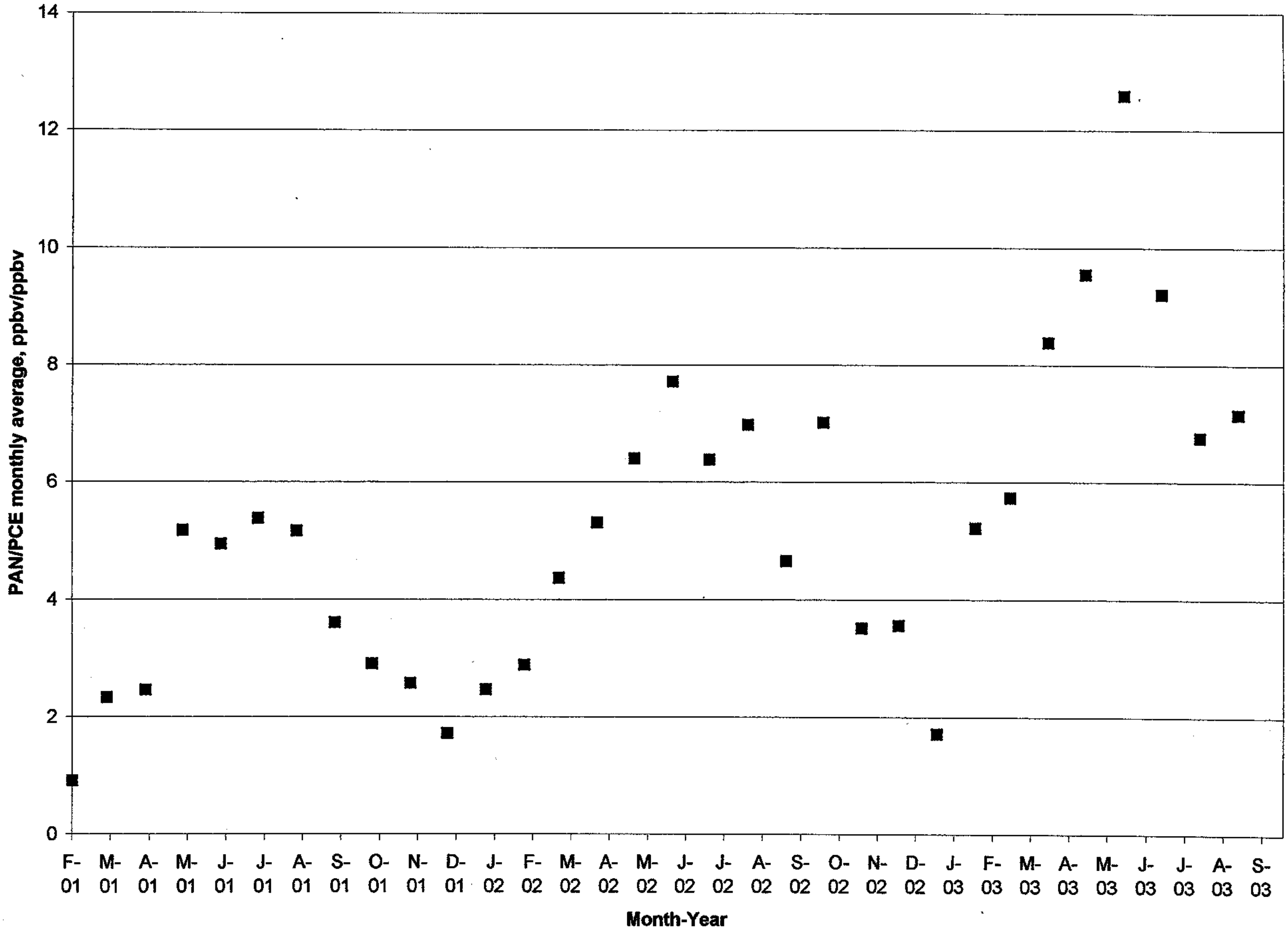

Figure 4.12 Monthly composite diurnal profiles for PCE, 2001

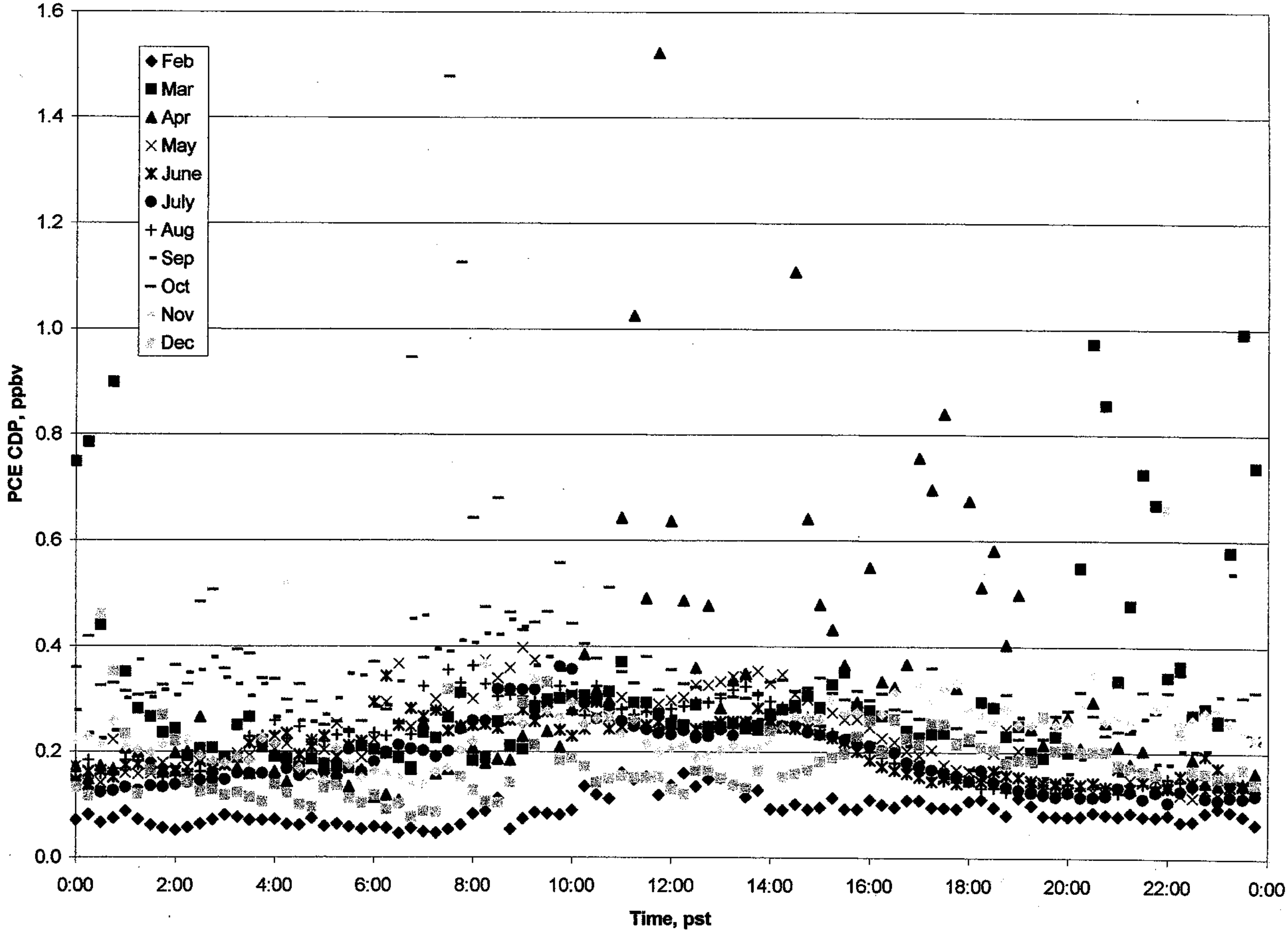

Figure 4.13 Monthly composite diurnal profiles for PCE, 2002

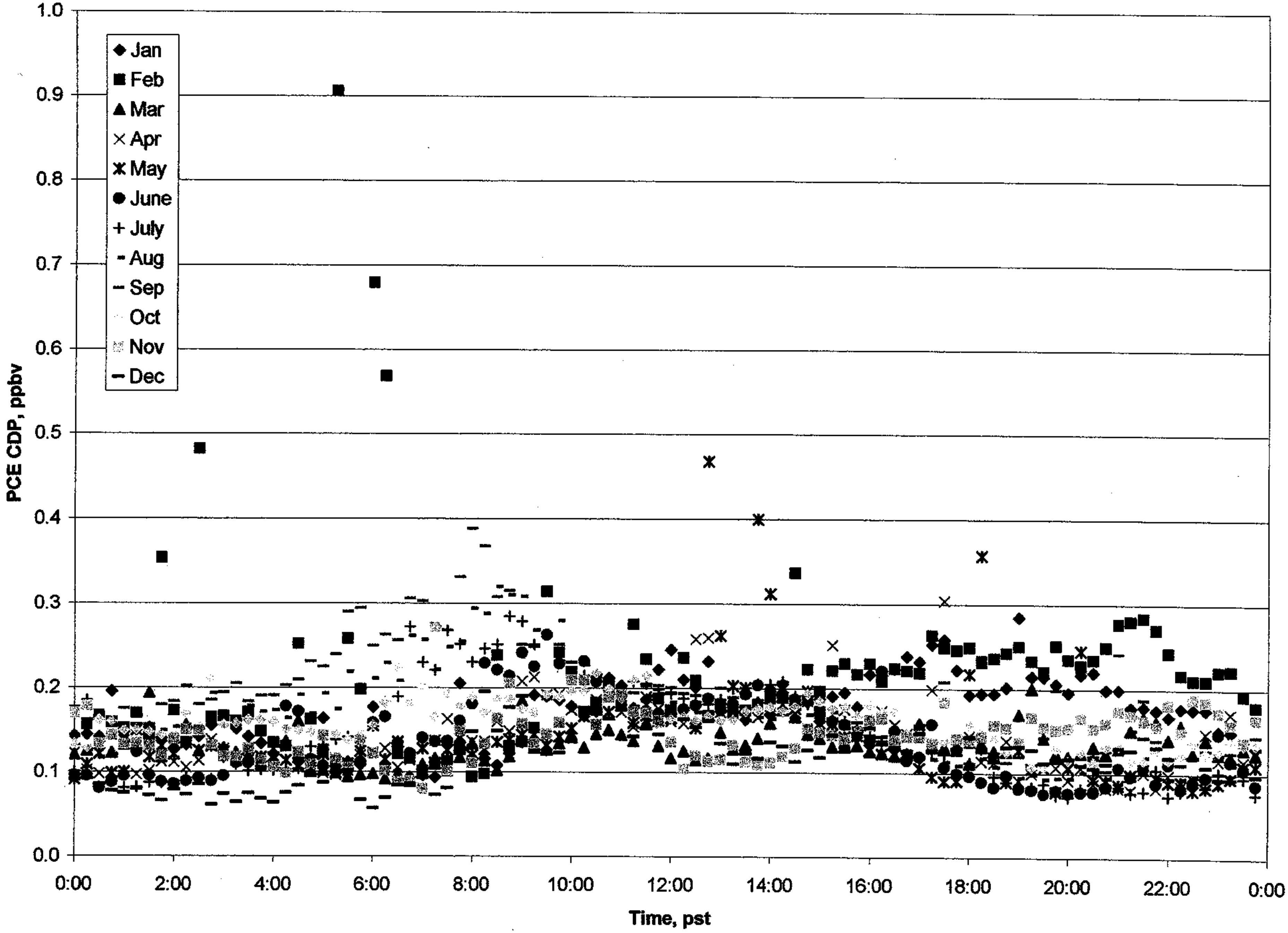

Figure 4.14 Monthly composite diurnal profiles for PCE, 2003

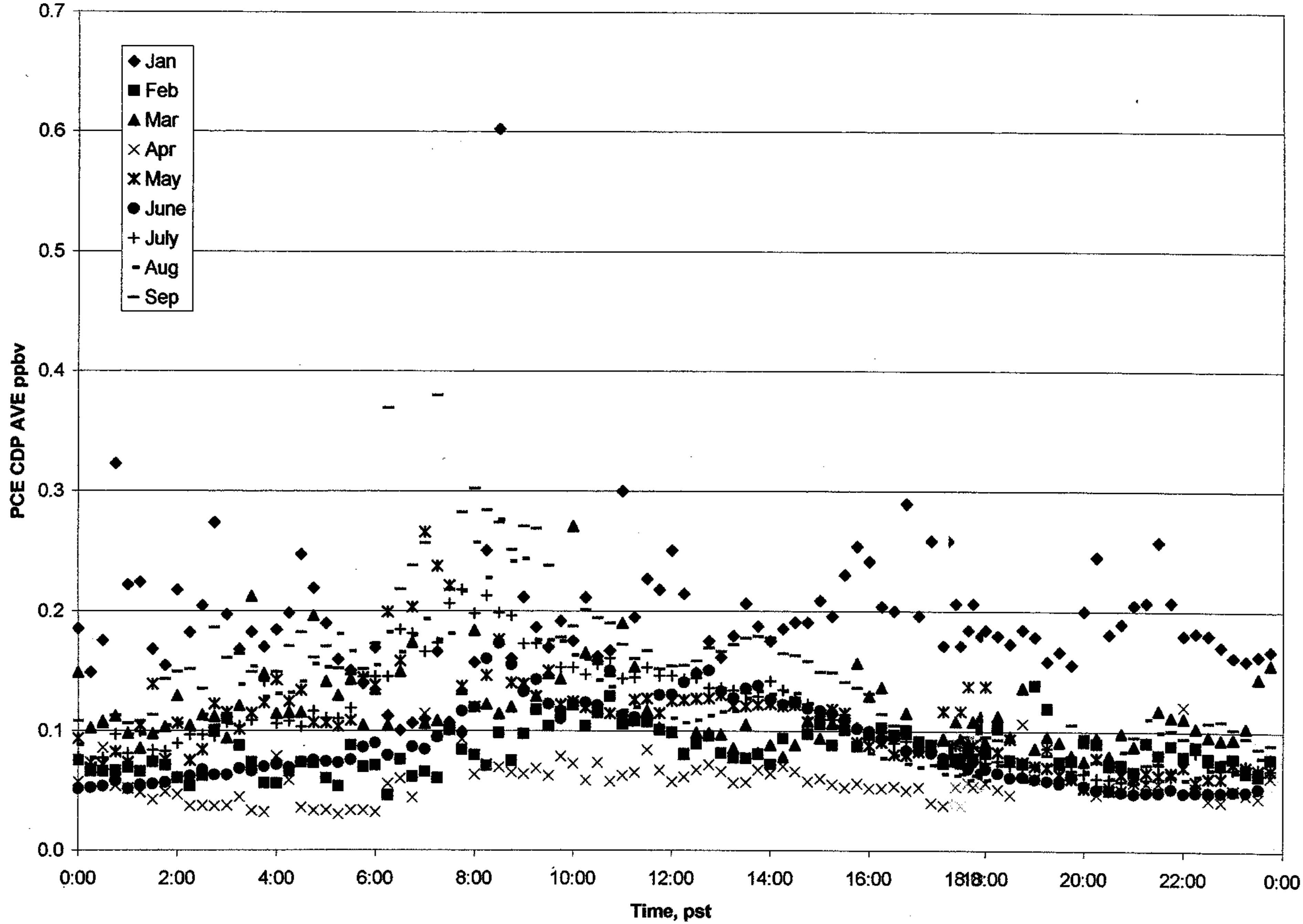

Figure 4.15 Study-averaged composite diurnal profiles for PAN and PPN

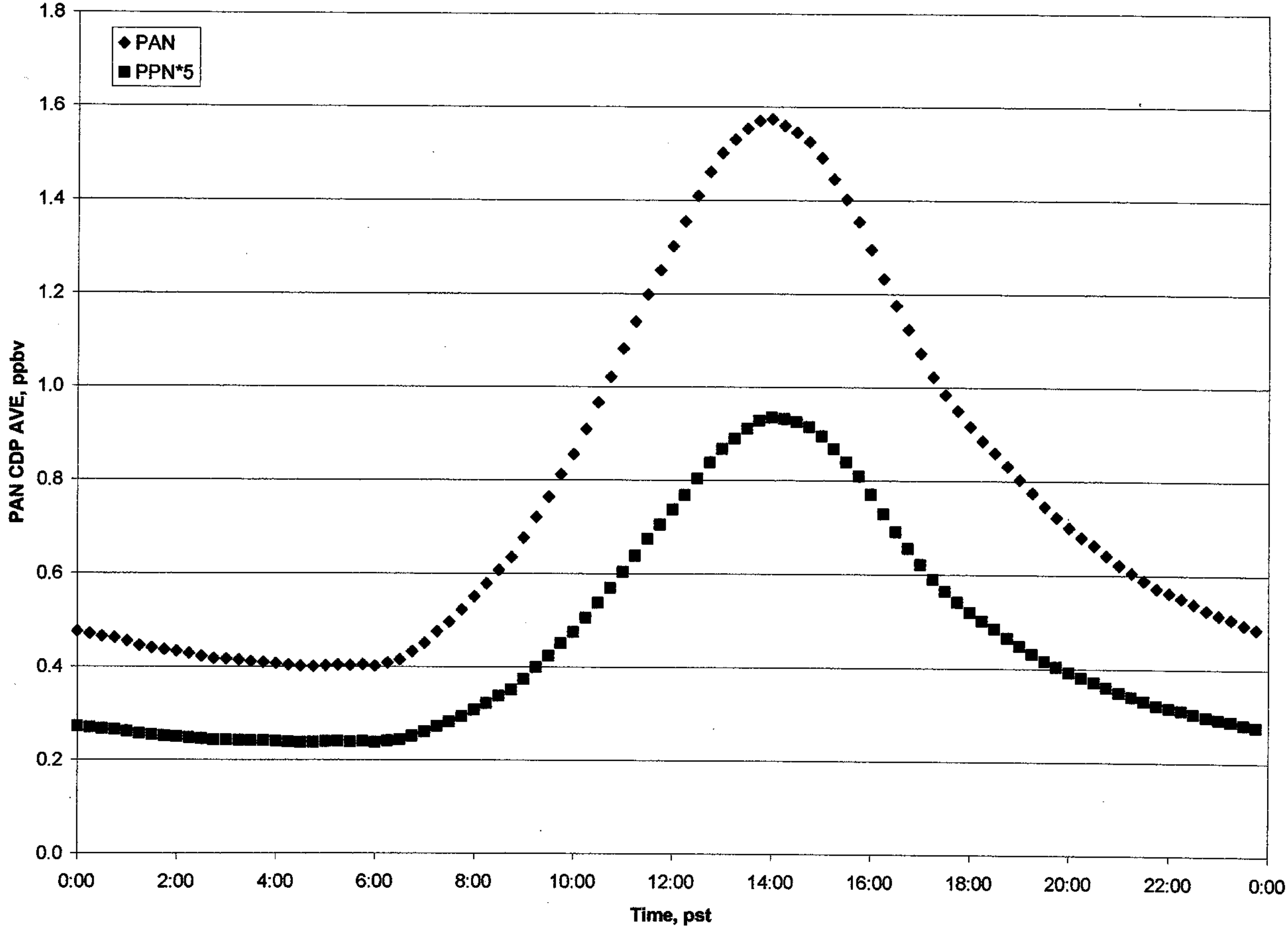

Figure 4.16 Yearly-averaged composite diurnal profiles for PAN, 2001, 2002 and 2003

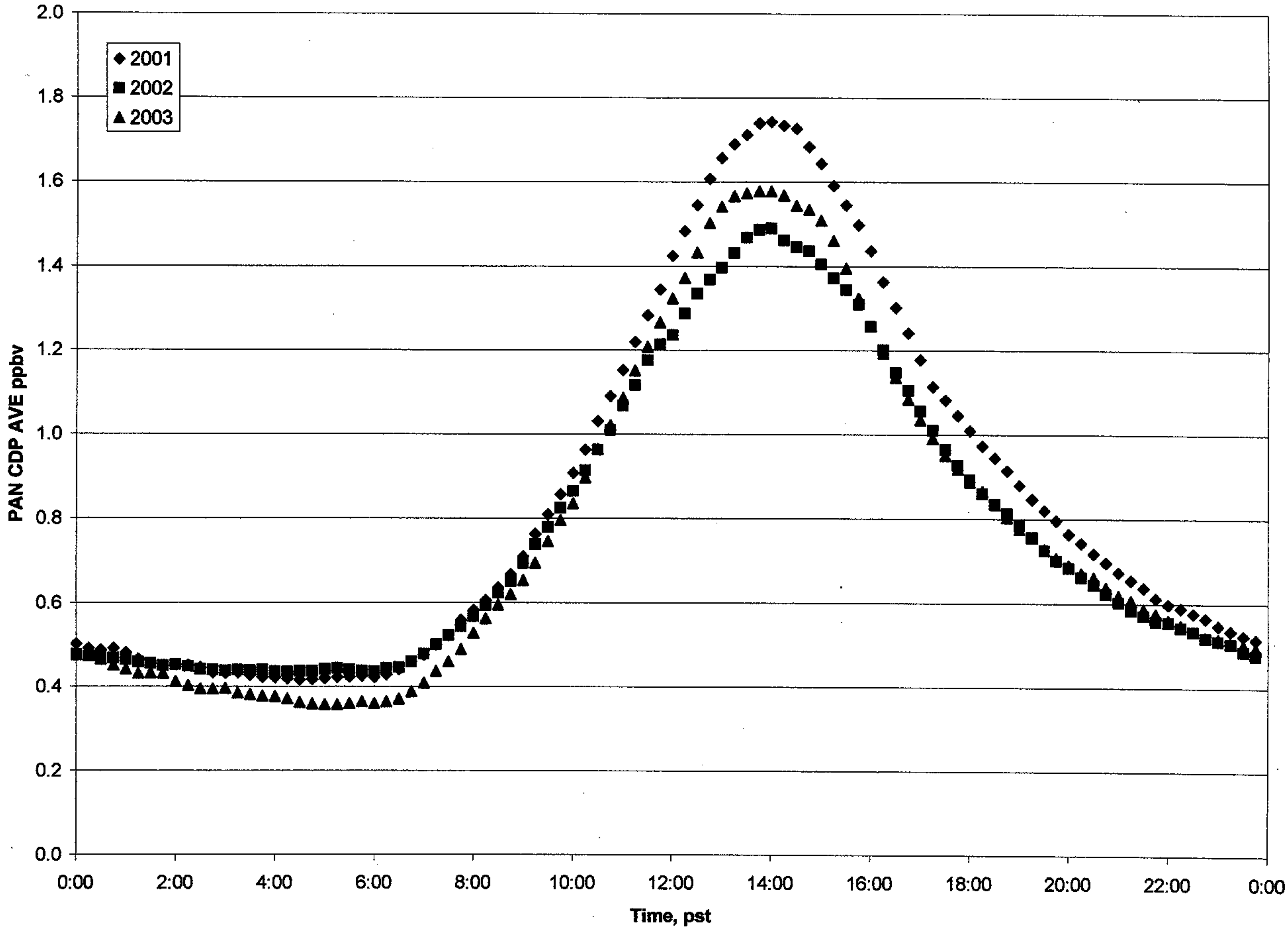

Figure 4.17 Composite diurnal profile with standard deviations for PAN, 2001

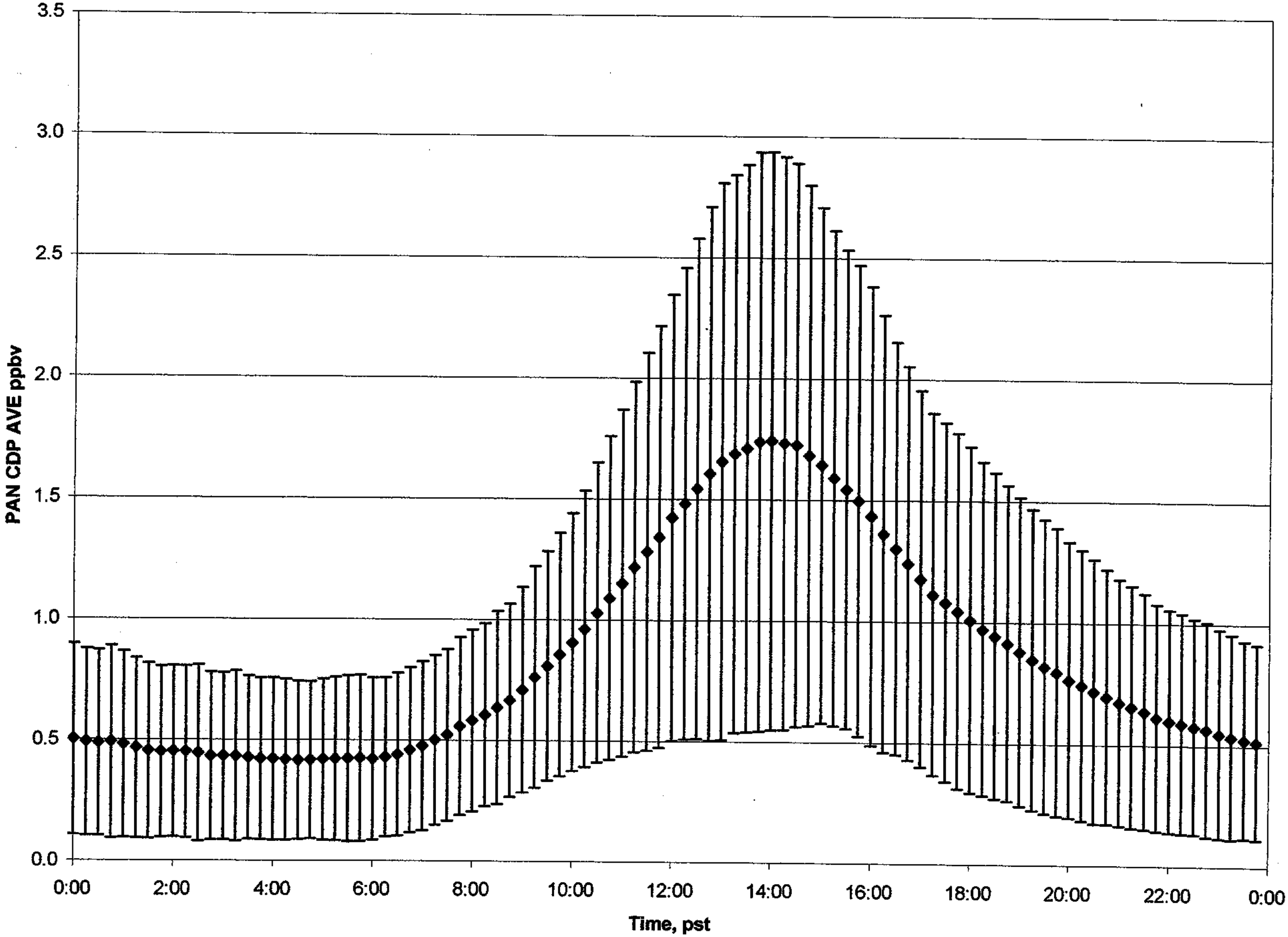

Figure 4.18 Composite diurnal profile with standard deviations for PAN, 2002

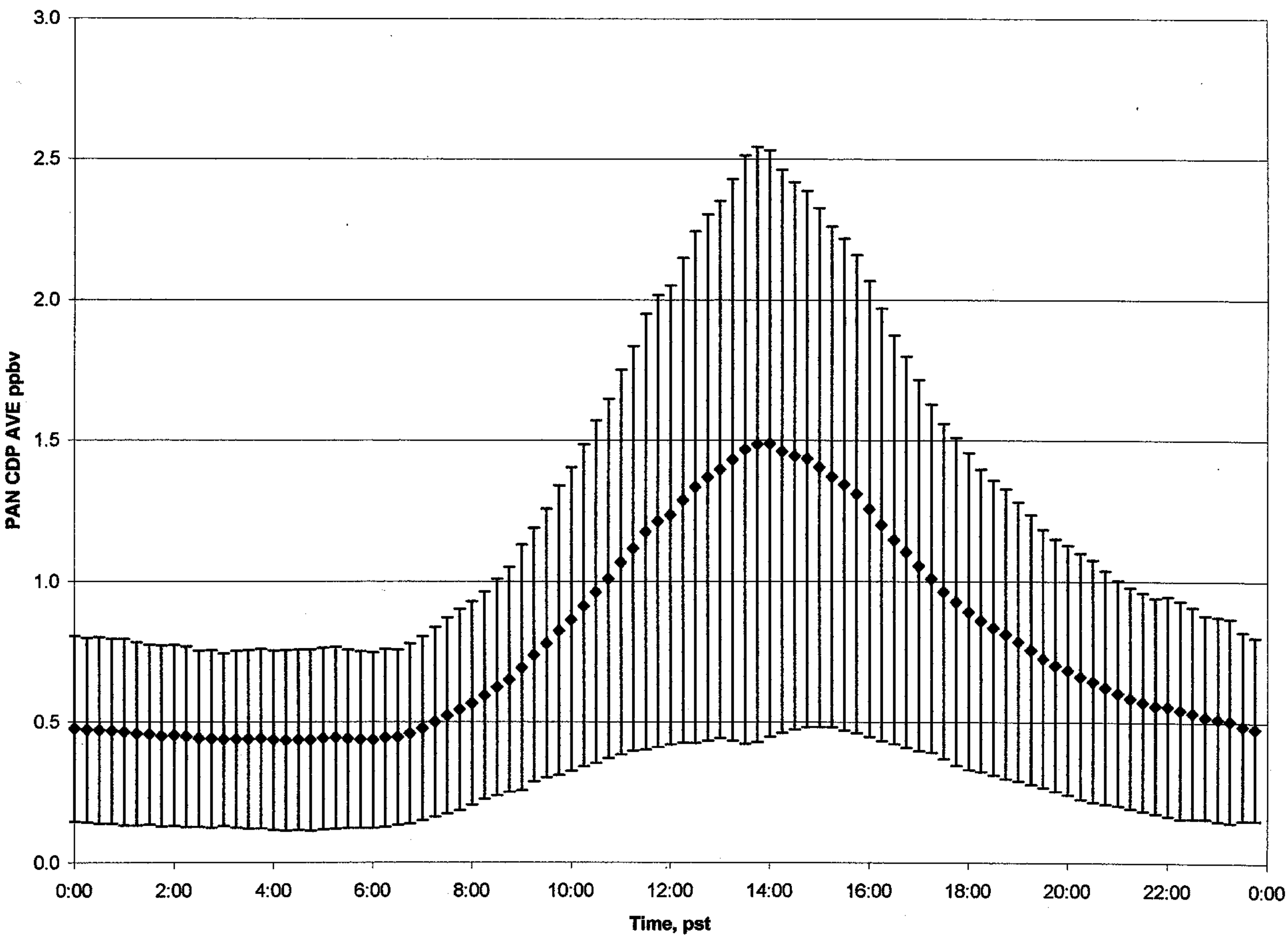

Figure 4.19 Composite diurnal profile with standard deviations for PAN, 2003

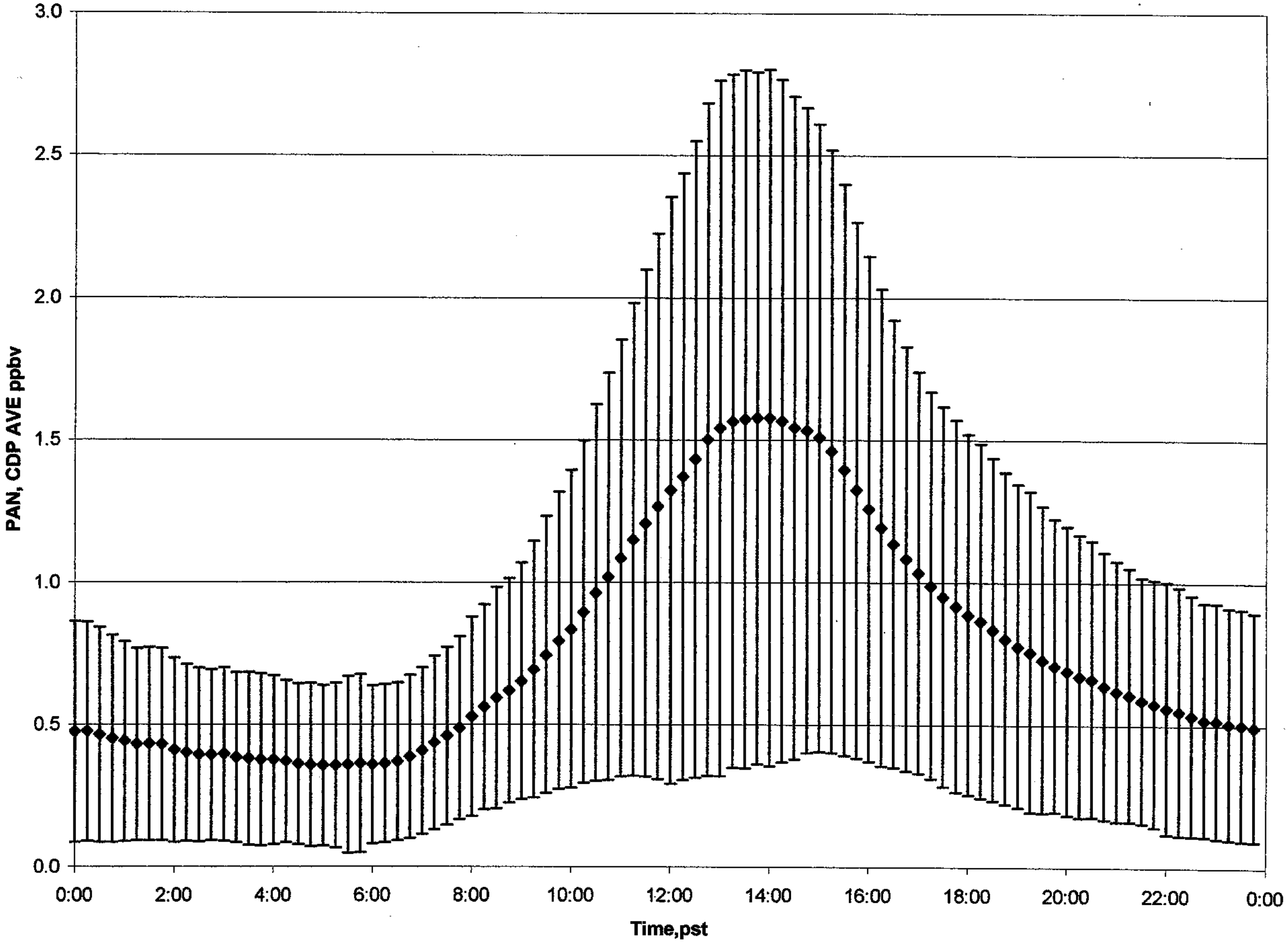

Figure 4.20 Study-averaged composite diurnal profile for PCE

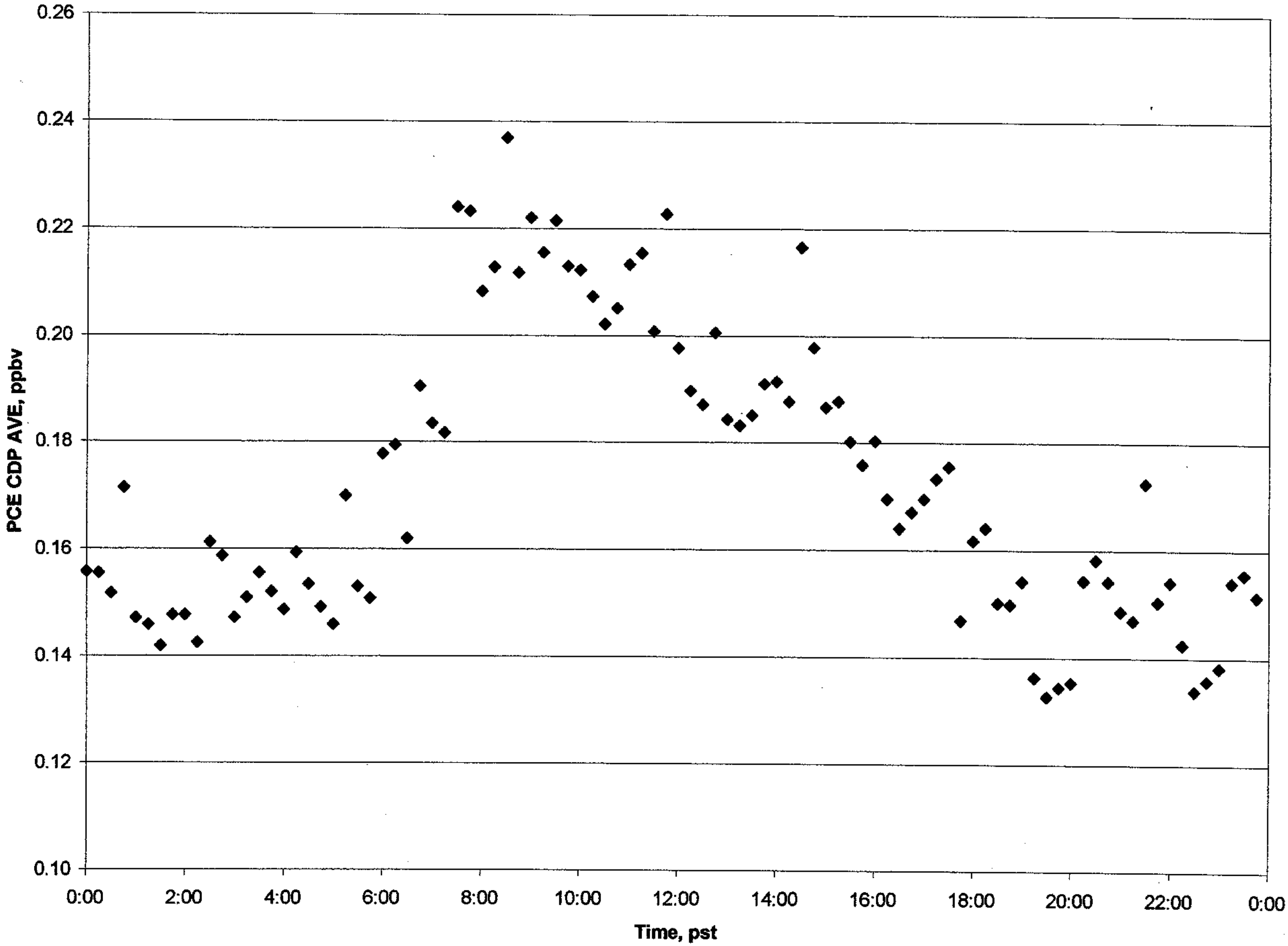

Figure 4.21 Yearly-averaged composite diurnal profiles for PCE, 2001, 2002 and 2003

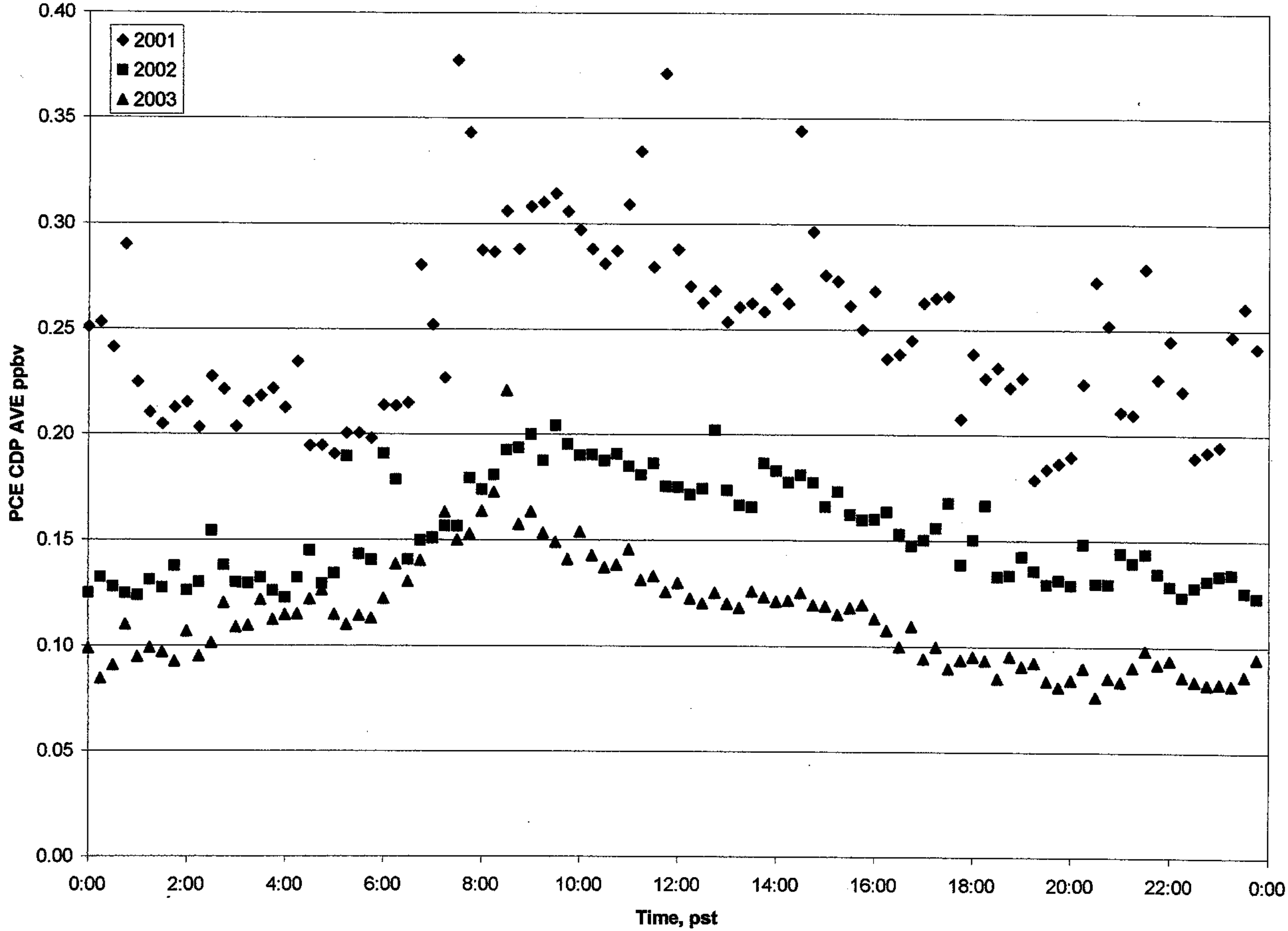

Figure 4.22 Composite diurnal profile for PCE, 2003

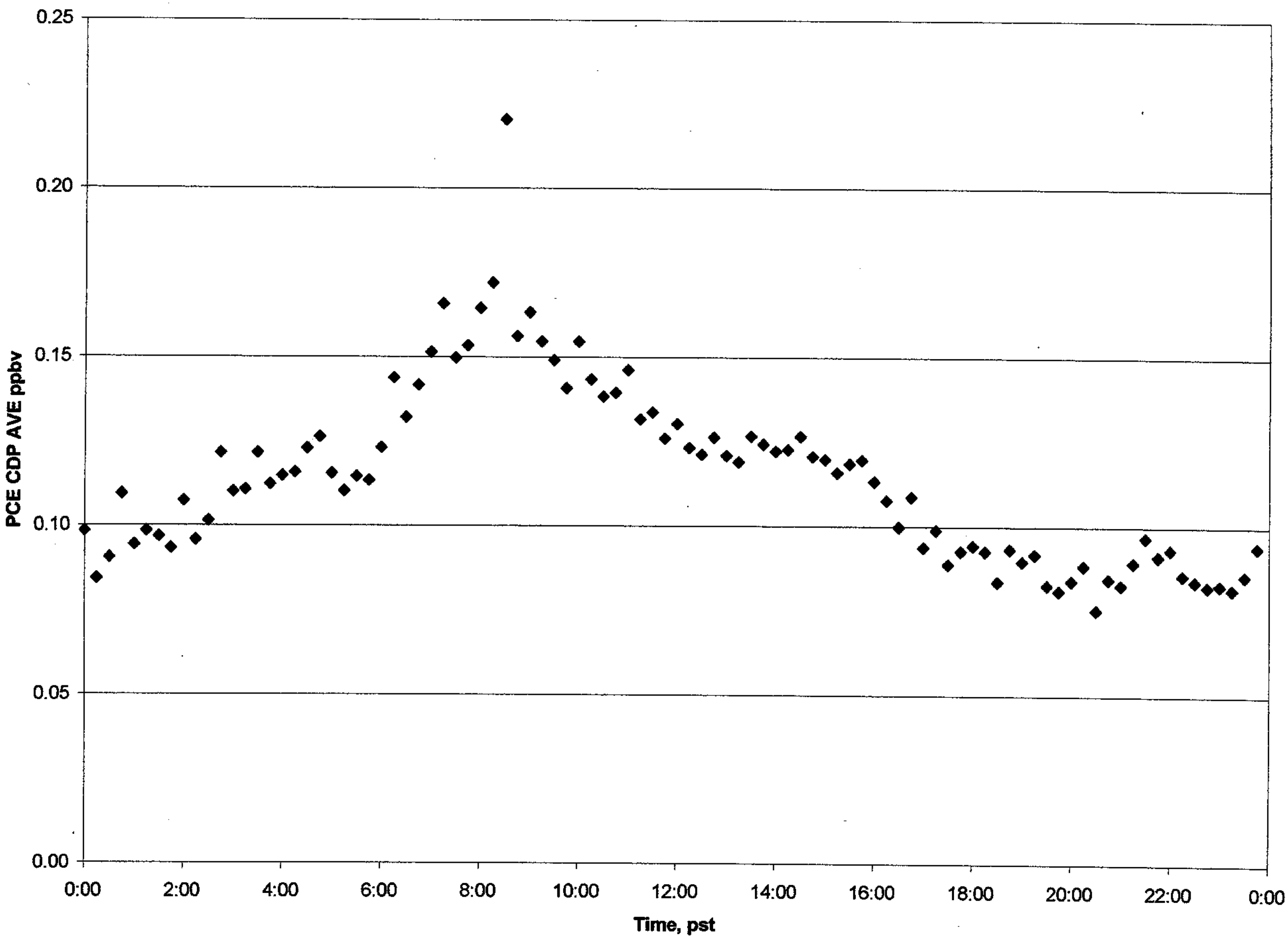

Figure 4.23 Composite diurnal profile with standard deviations for PCE, 2003

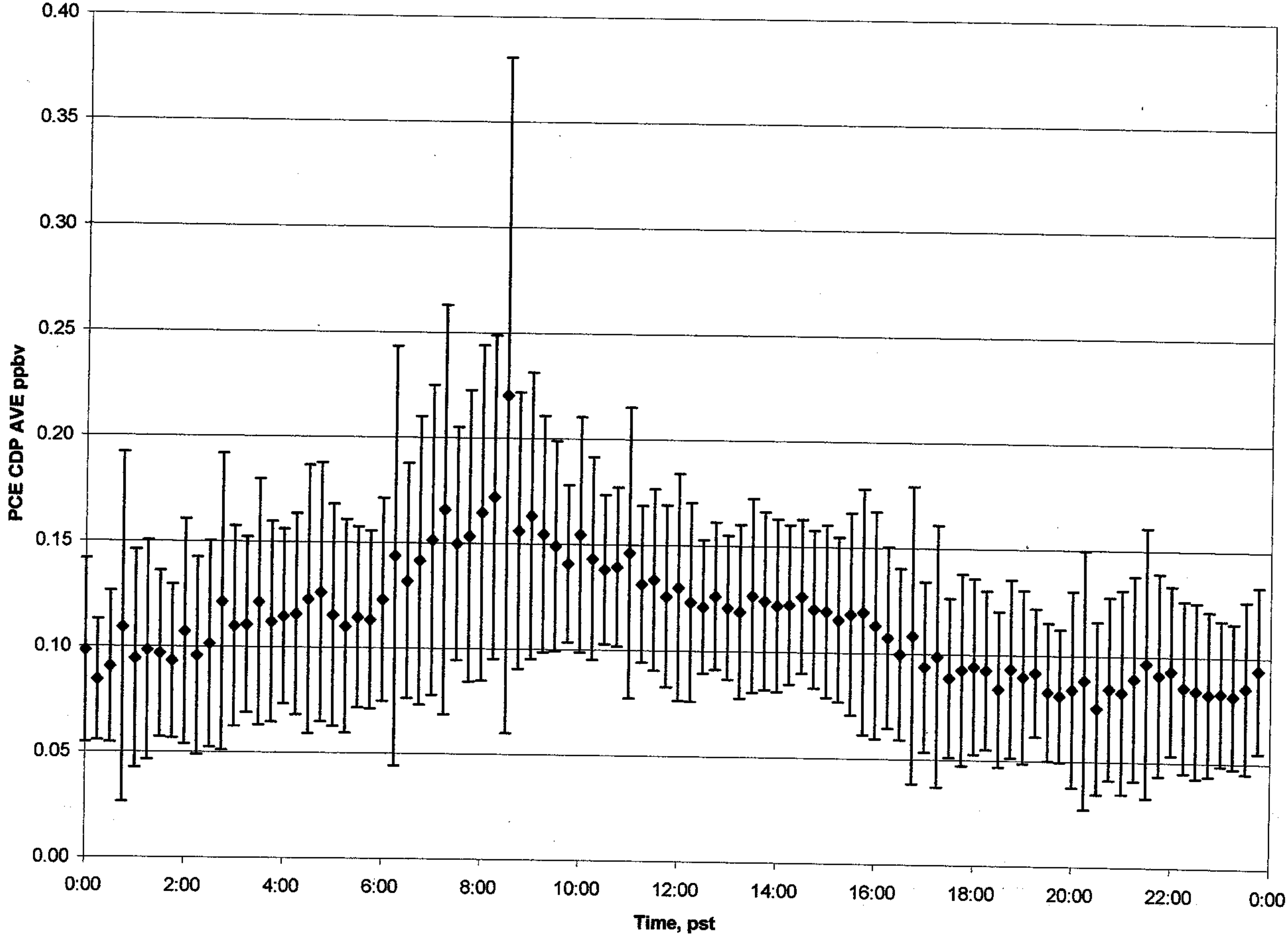

Figure 4.24 Study-averaged composite diurnal profile for the PCE/PAN concentration ratio

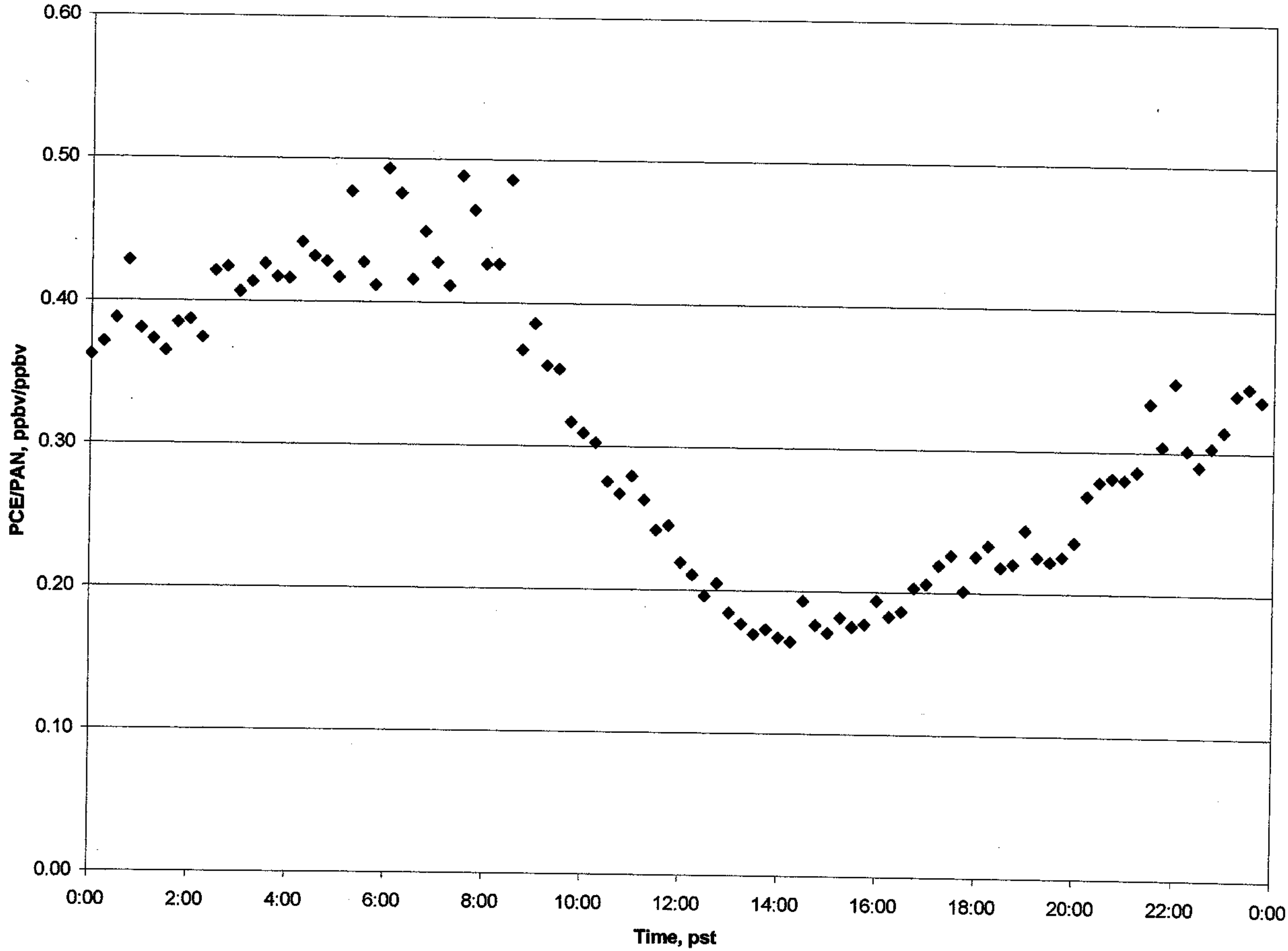

Figure 4.25 Scatterplot of ambient PCE concentrations measured every 15 minutes vs. those measured by ARB in 24-hour samples

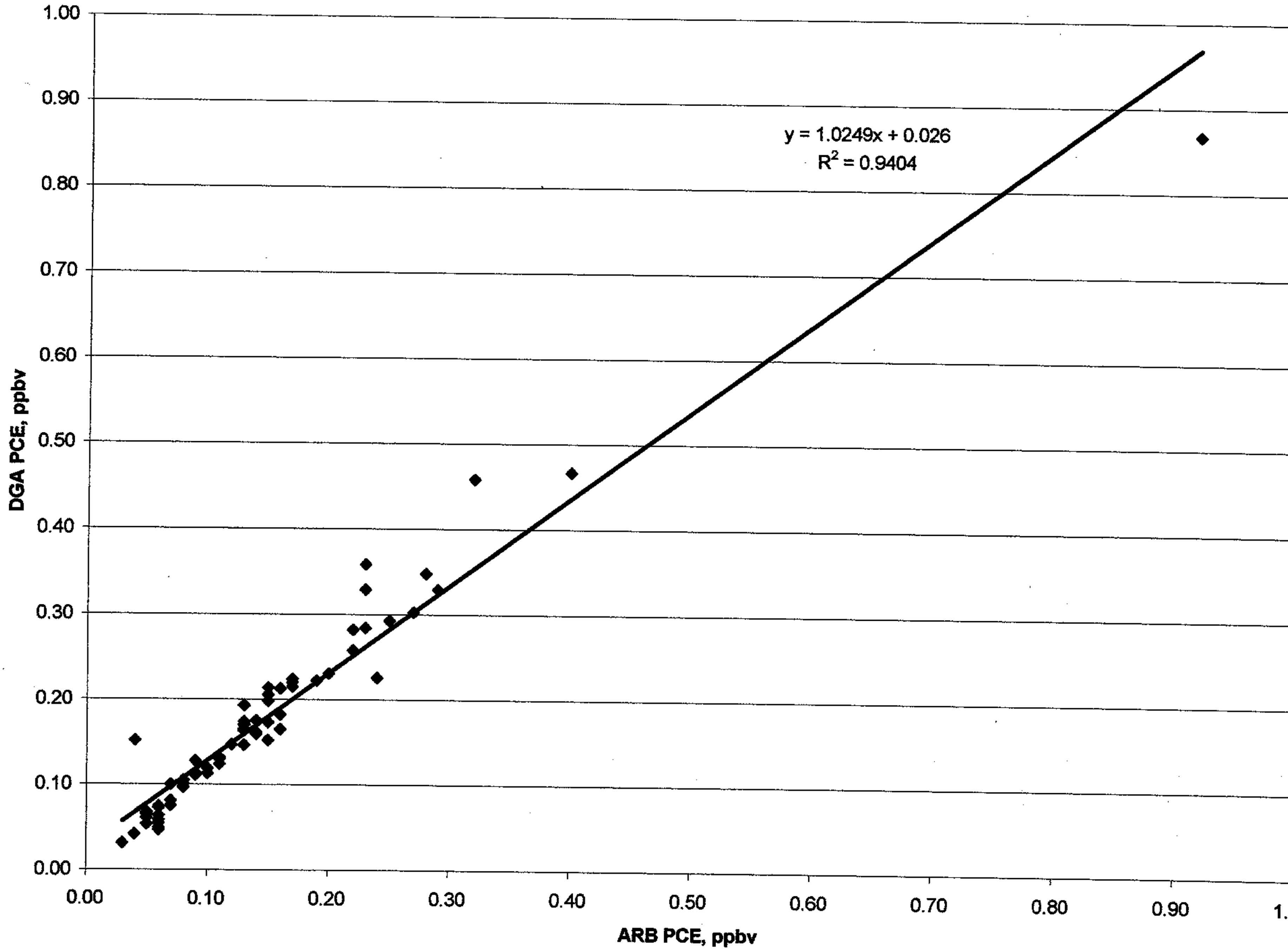

Figure 5.1 Composite diurnal profiles of PAN concentrations for each day of the week in 2002

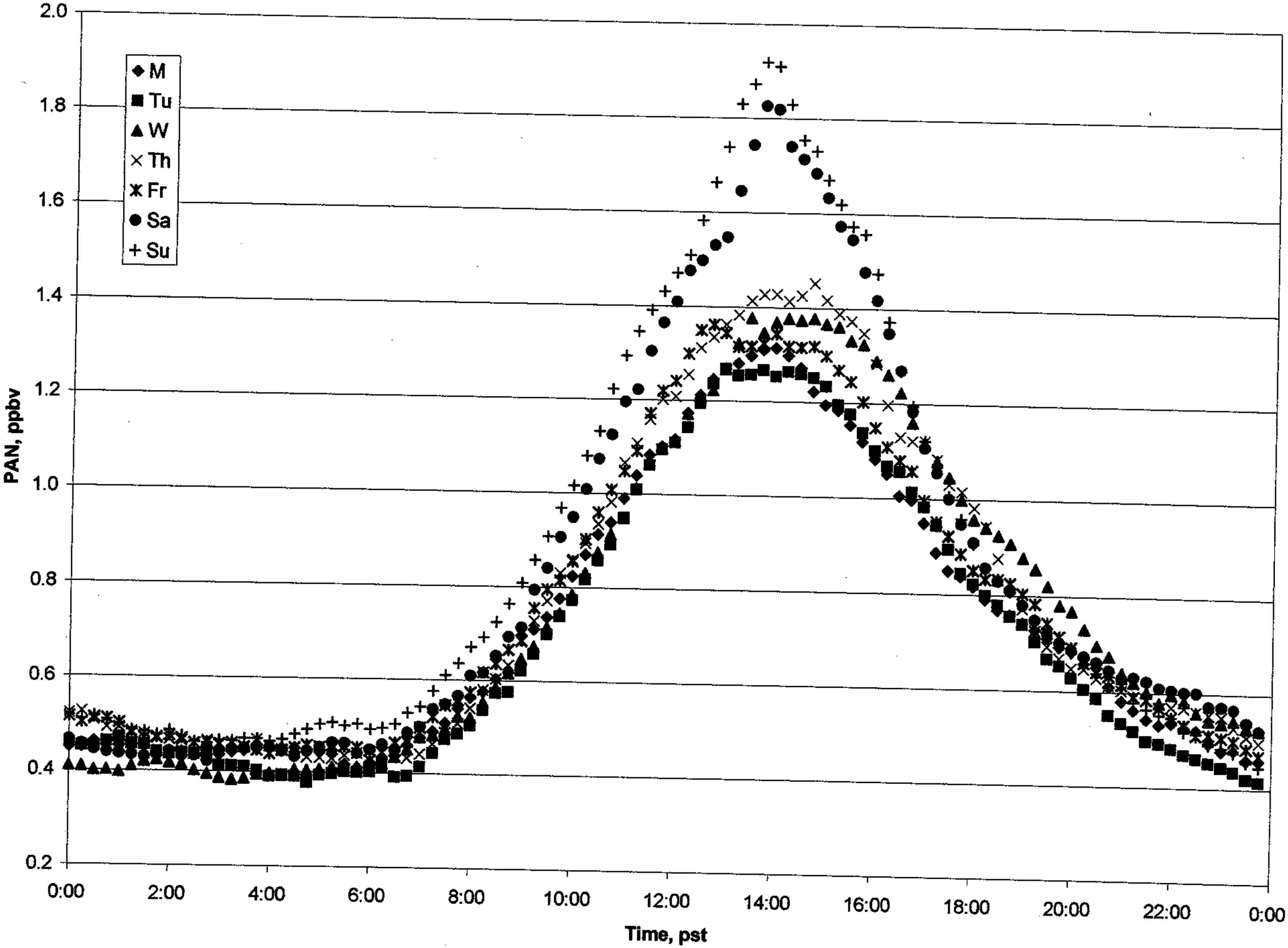

Figure 5.2 Composite diurnal profiles of PAN concentrations for each day of the week in 2002, 9 a.m. to 5 p.m.

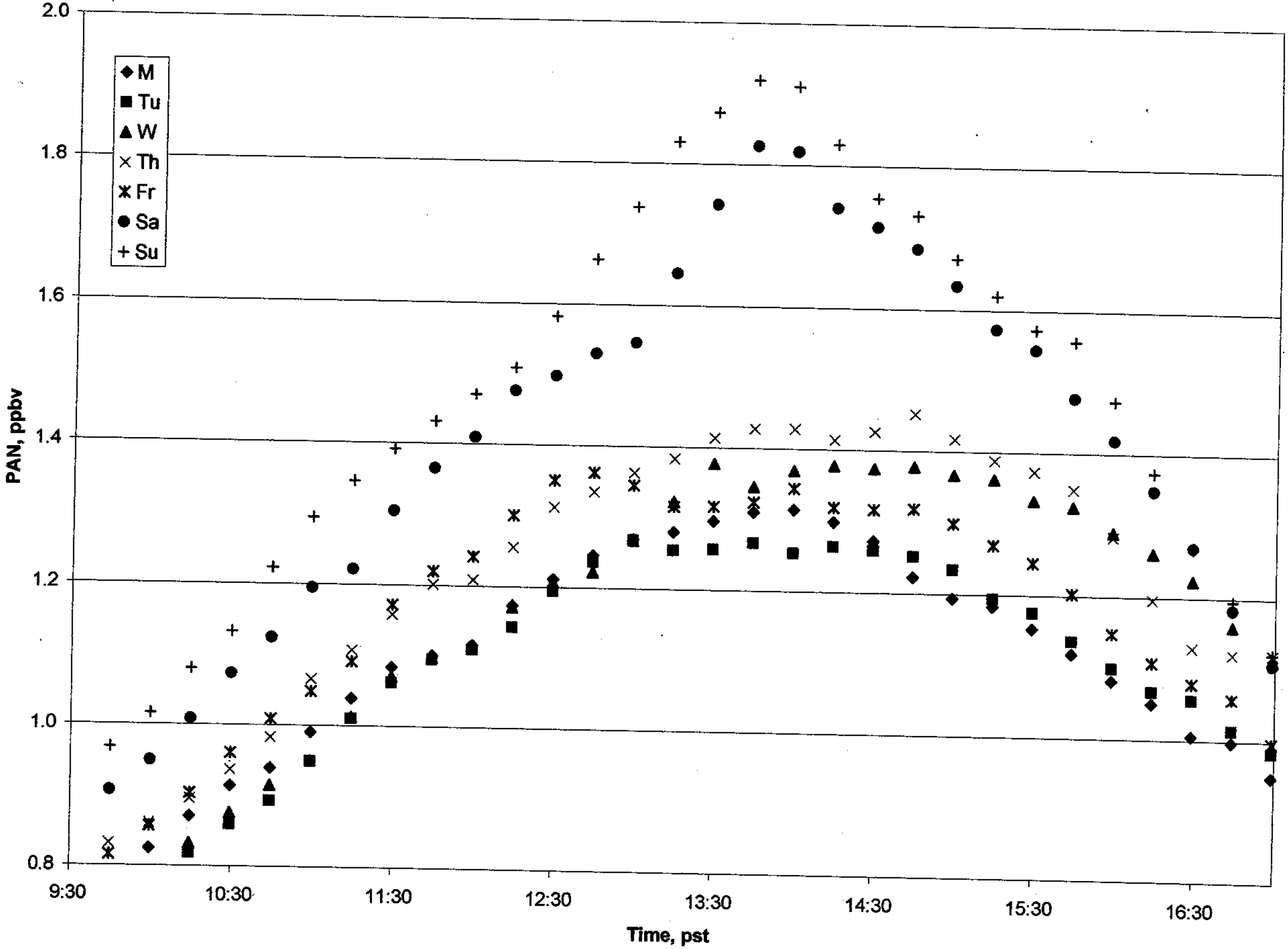

Figure 5.3 Composite diurnal profile of PCE concentrations for each day of the week in 2002

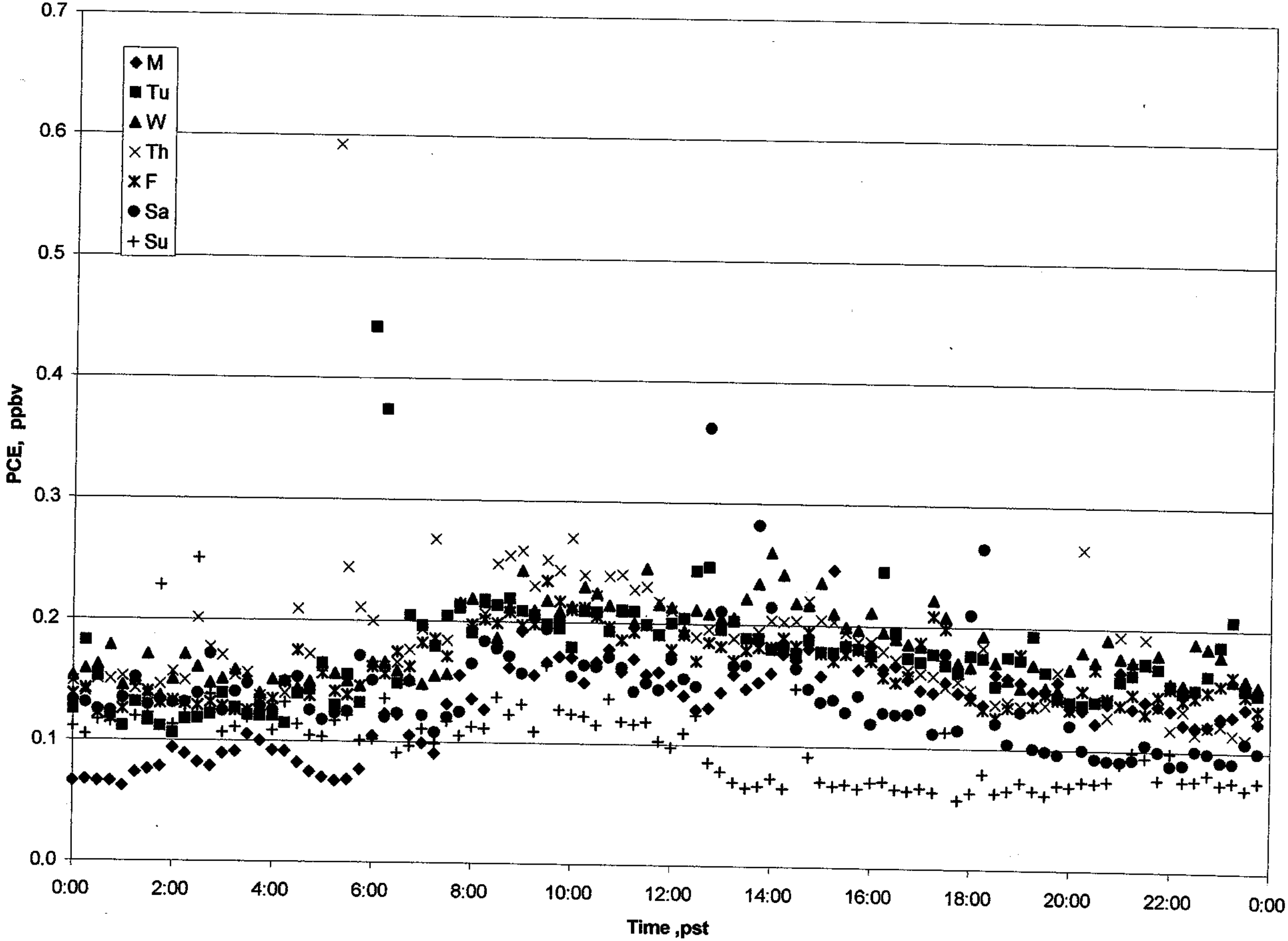

Figure 5.4 Time series plot of PAN minima, February 2001 – September 2002

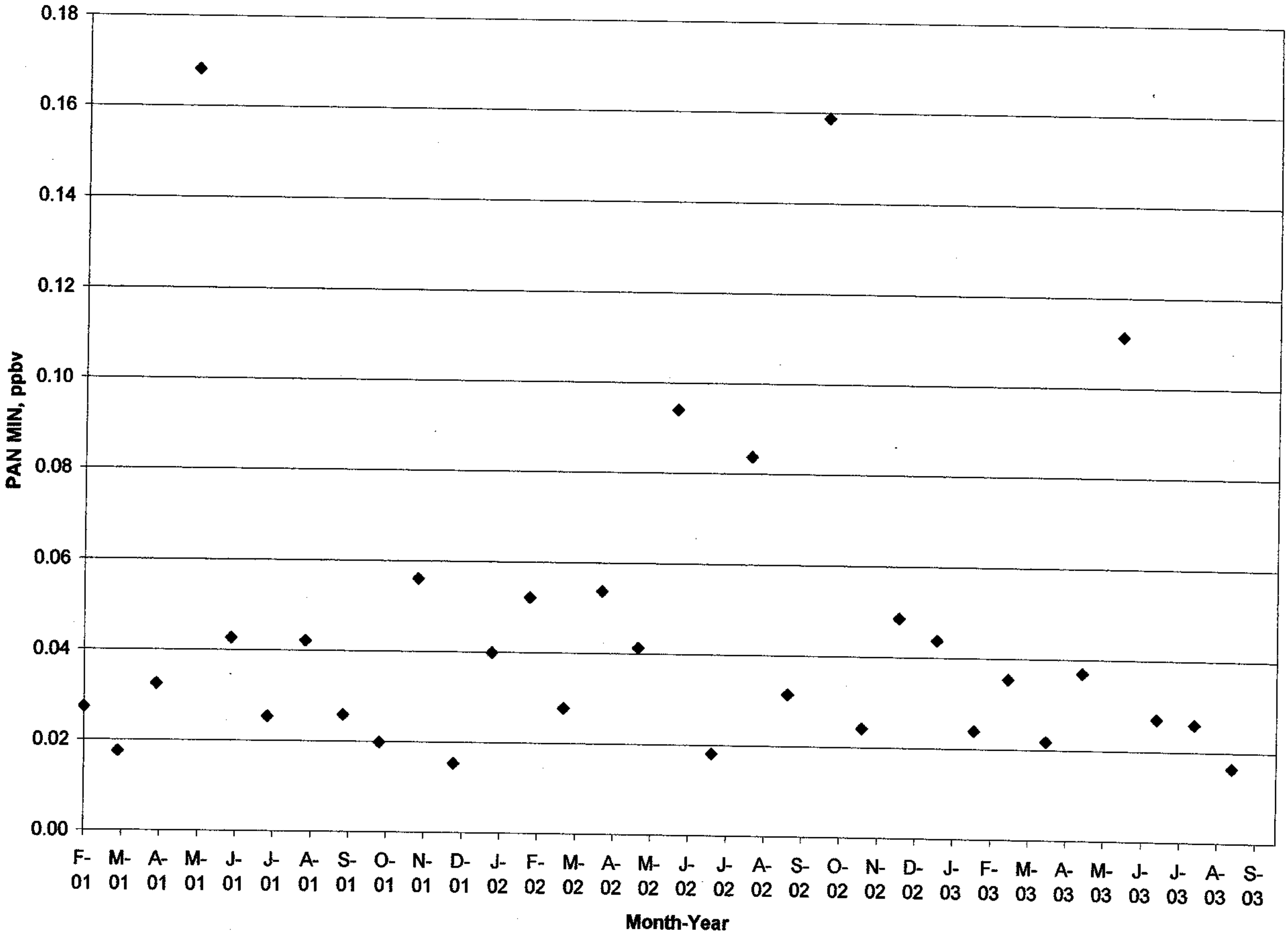

Figure 5.5 Composite diurnal profiles of PAN minima for 2001, 2002 and 2003

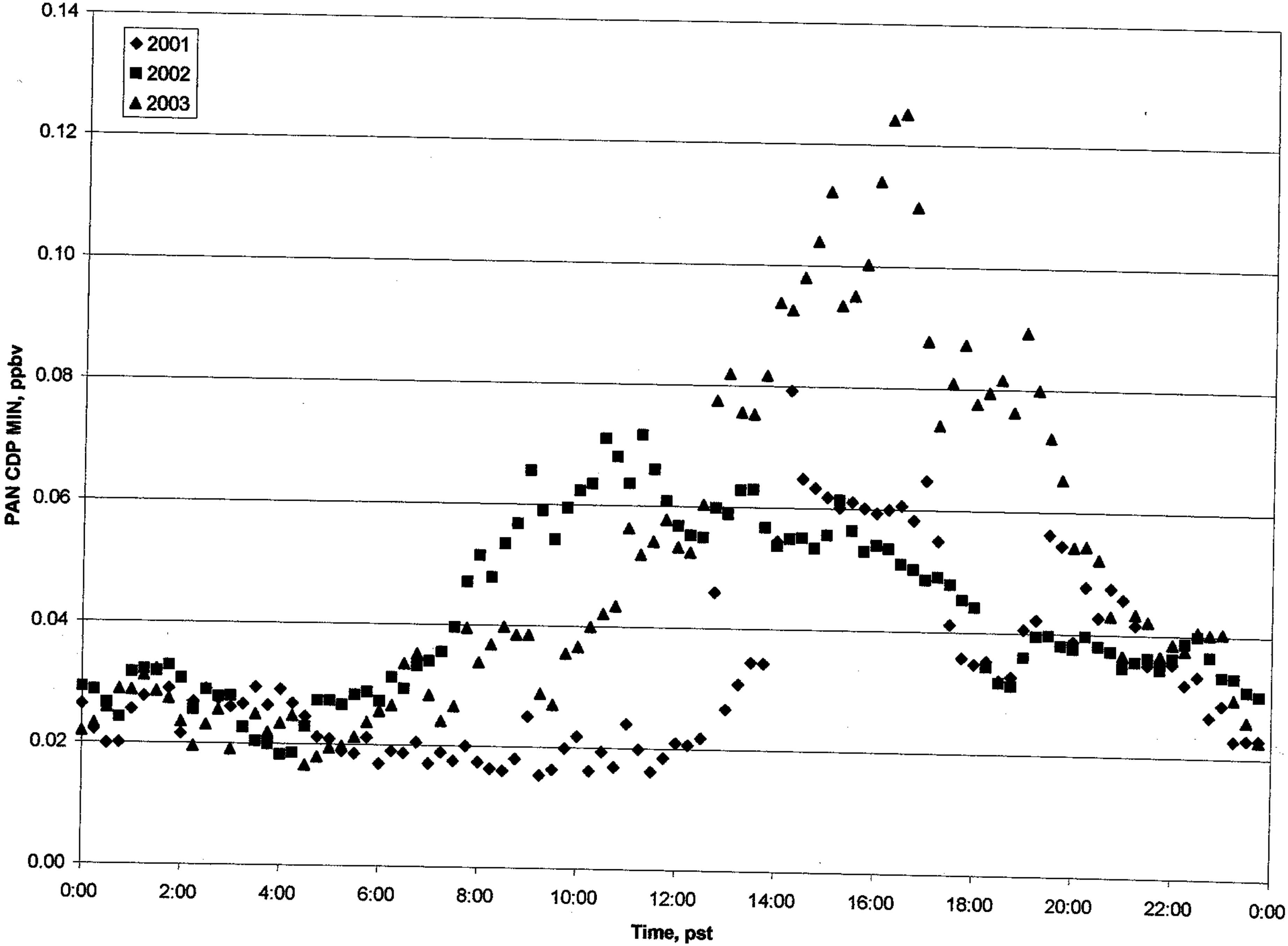

Figure 5.6 Composite diurnal profiles of PCE minima for 2001, 2002 and 2003

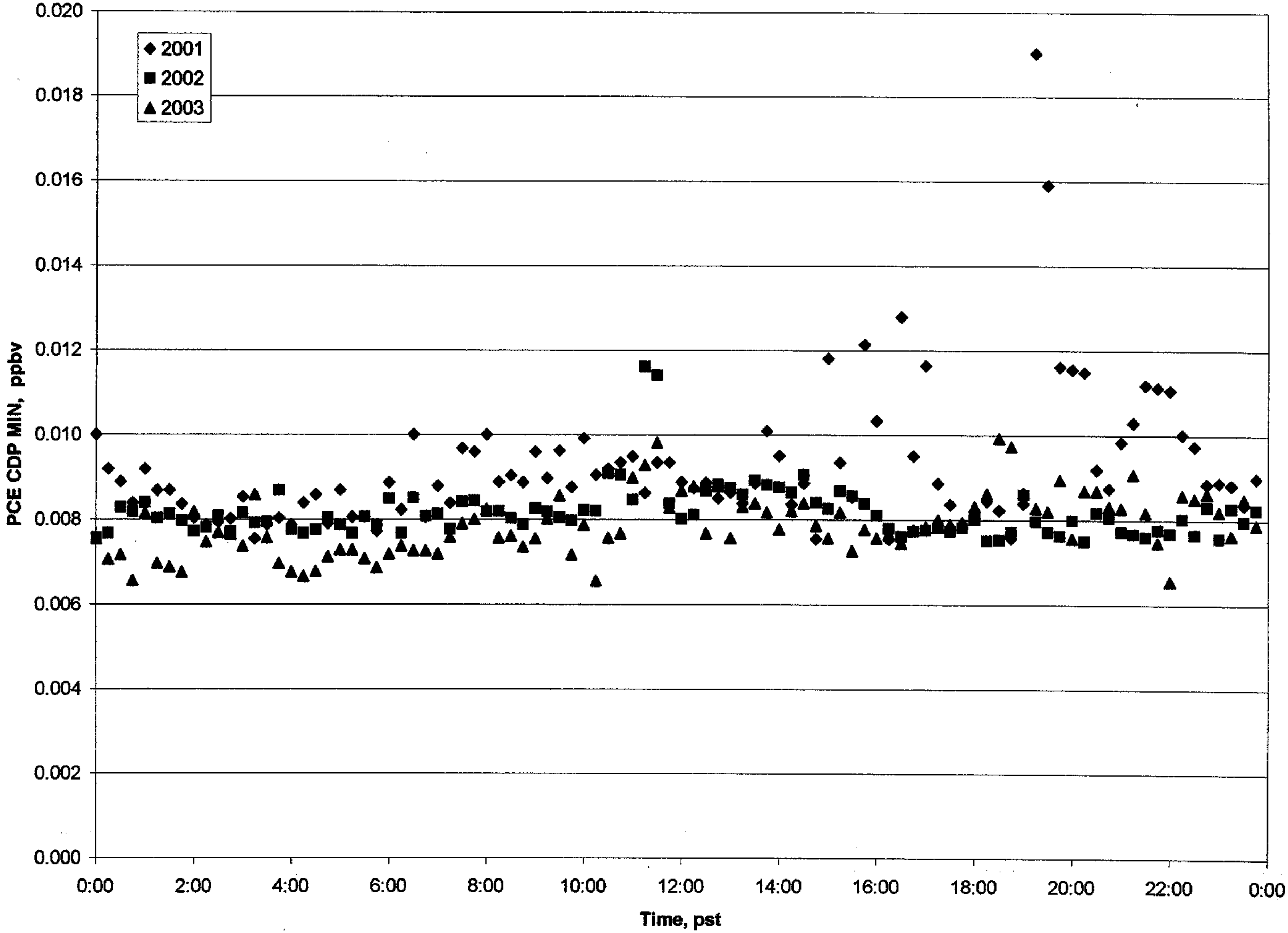

Figure 5.7 Ambient concentration of PCE, November 29, 2001

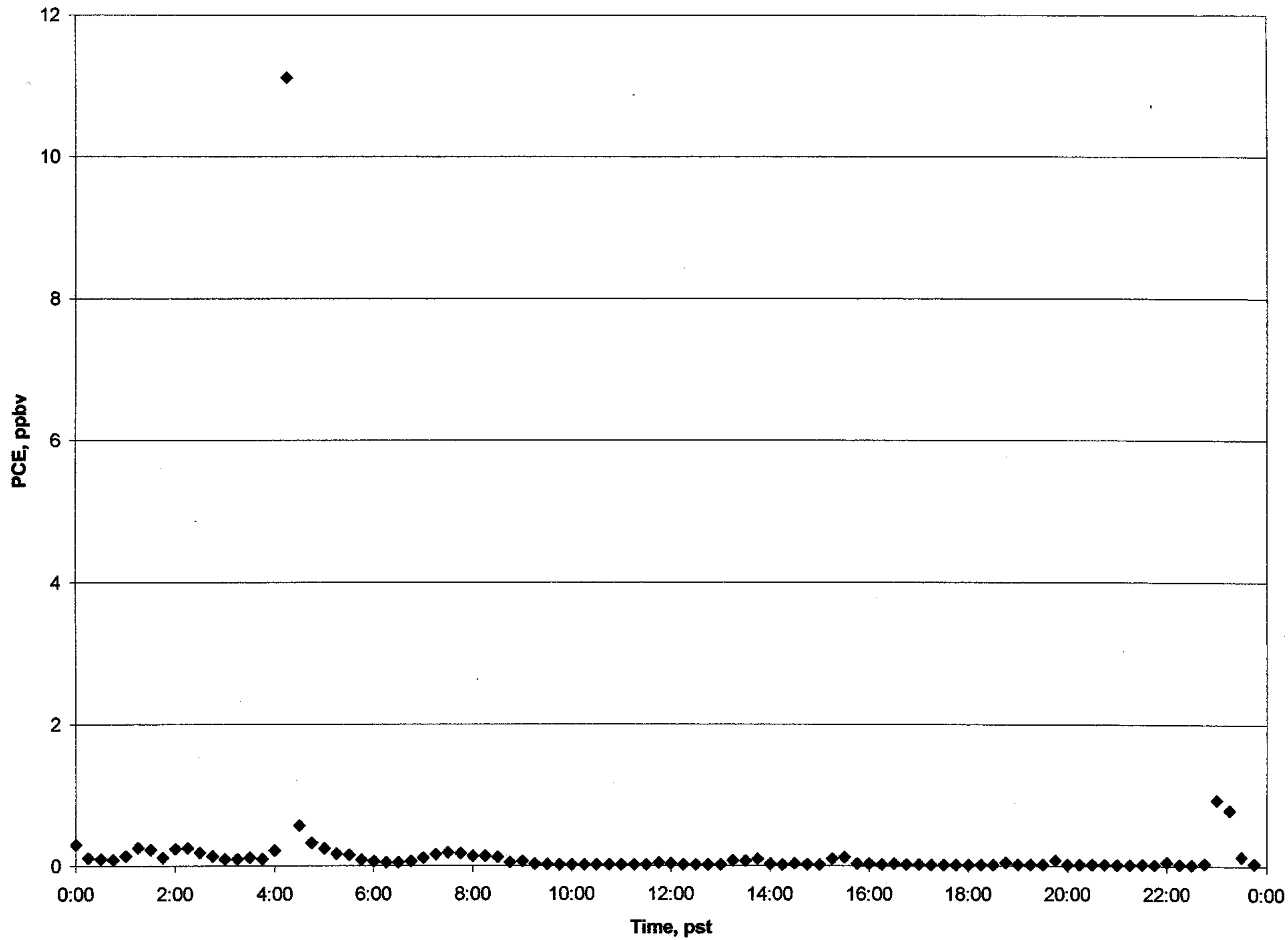

Figure 5.8 Ambient concentration of PCE, March 30 – 31, 2001

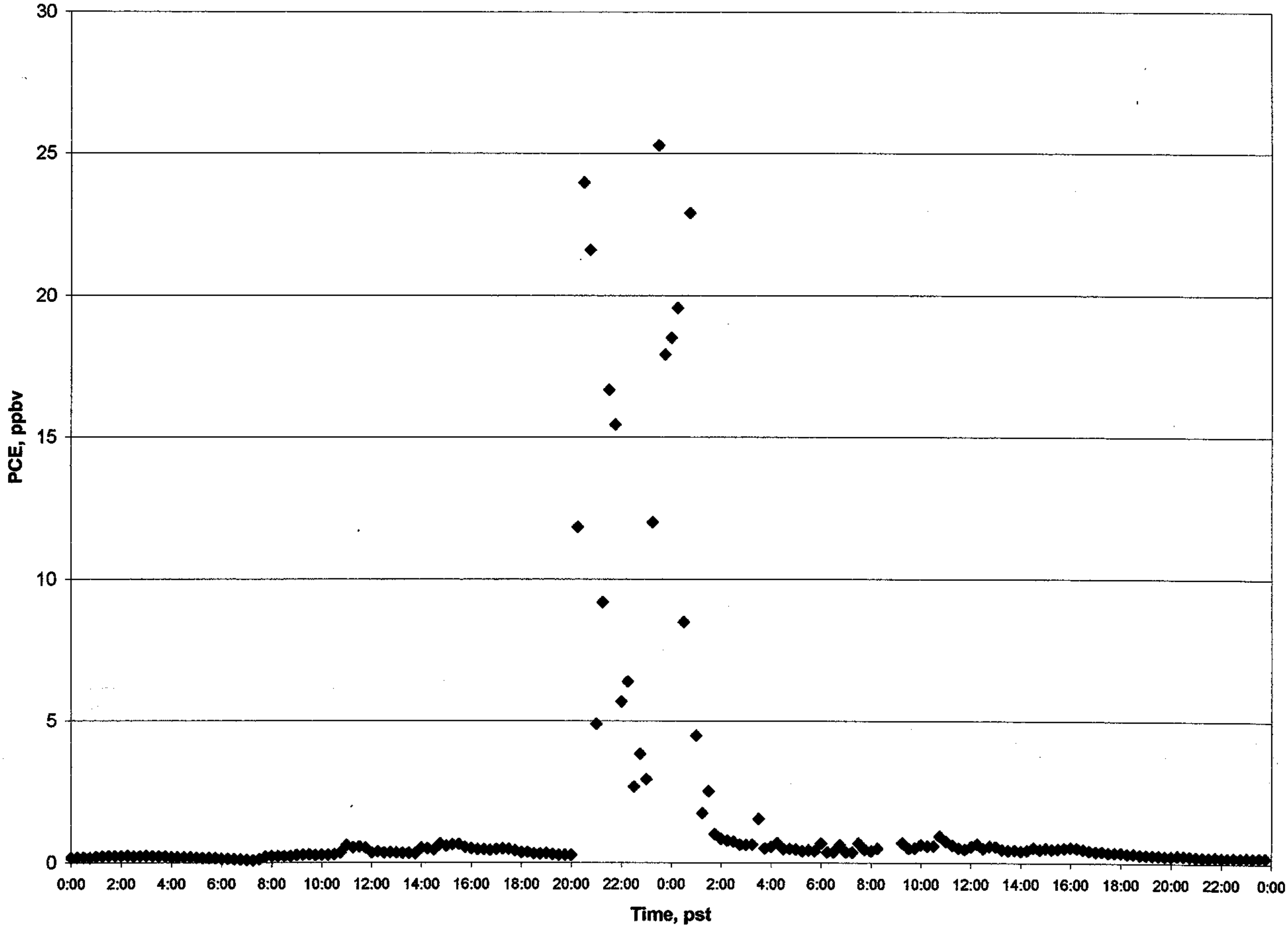

Figure 5.9 Ambient concentration of PCE, October 26, 2001

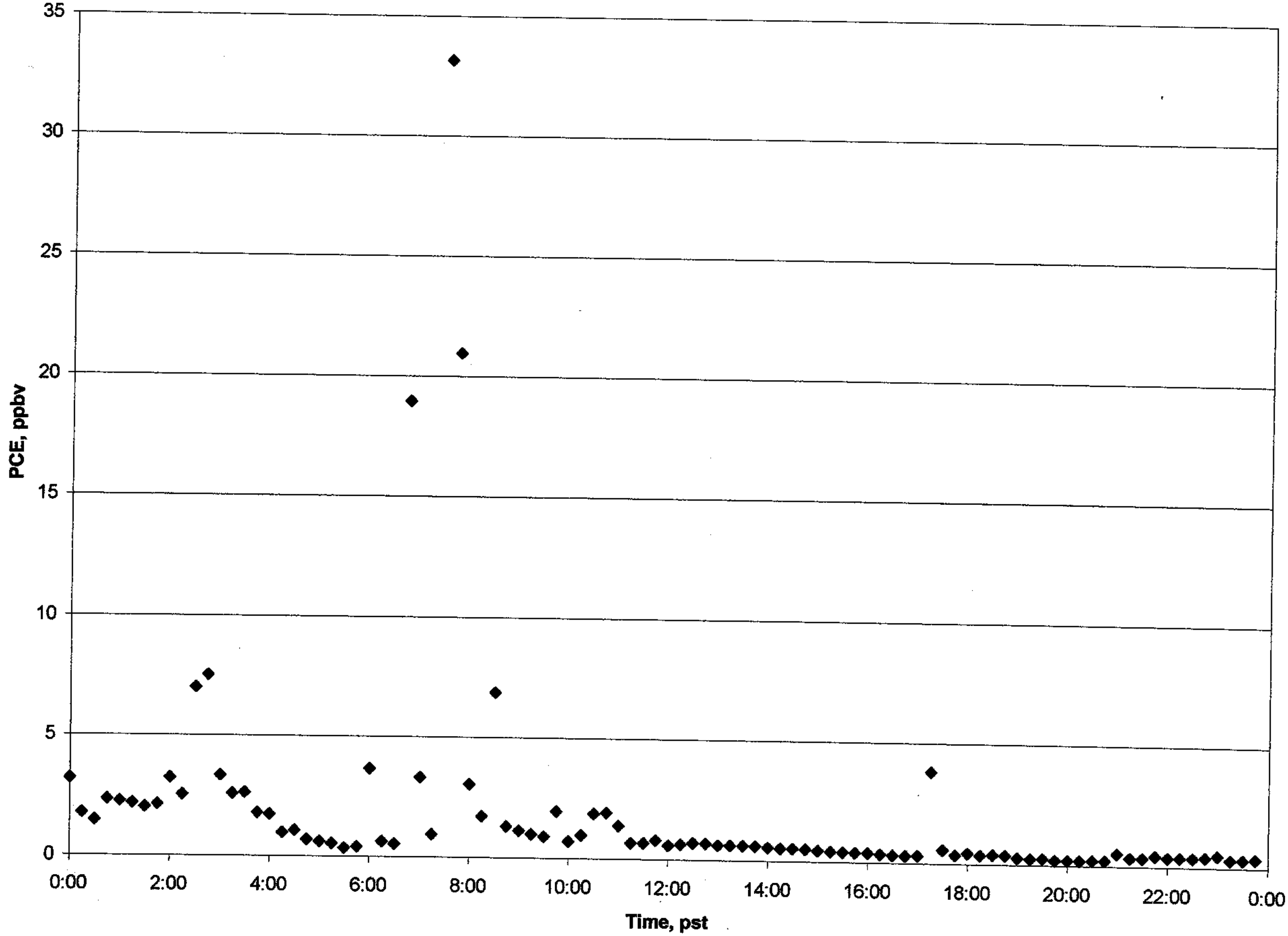

Figure 5.10 Ambient concentration of PCE, April 29, 2001

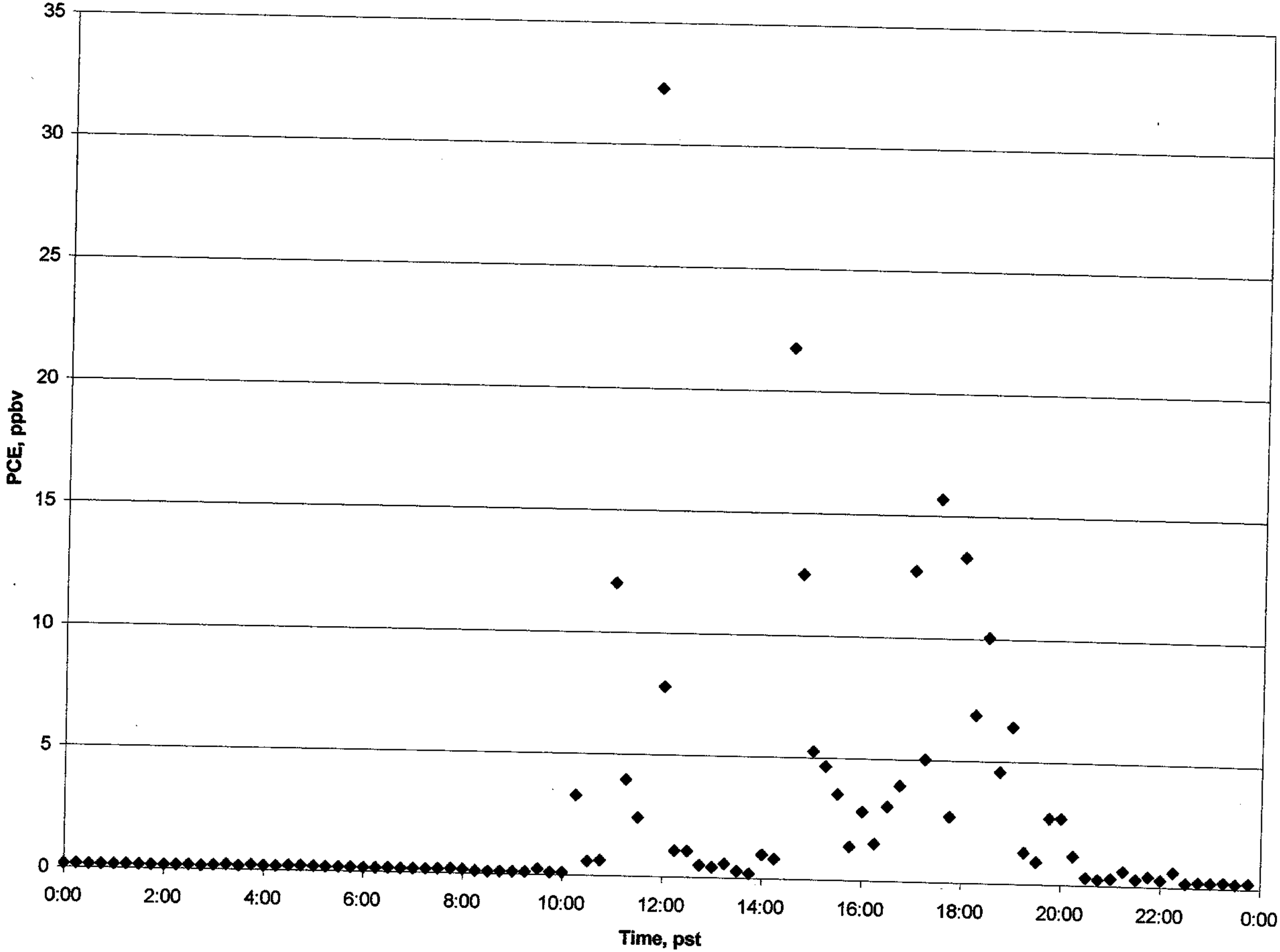

Figure 5.11 Ambient concentration of PAN and PPN, March 30 –31, 2001

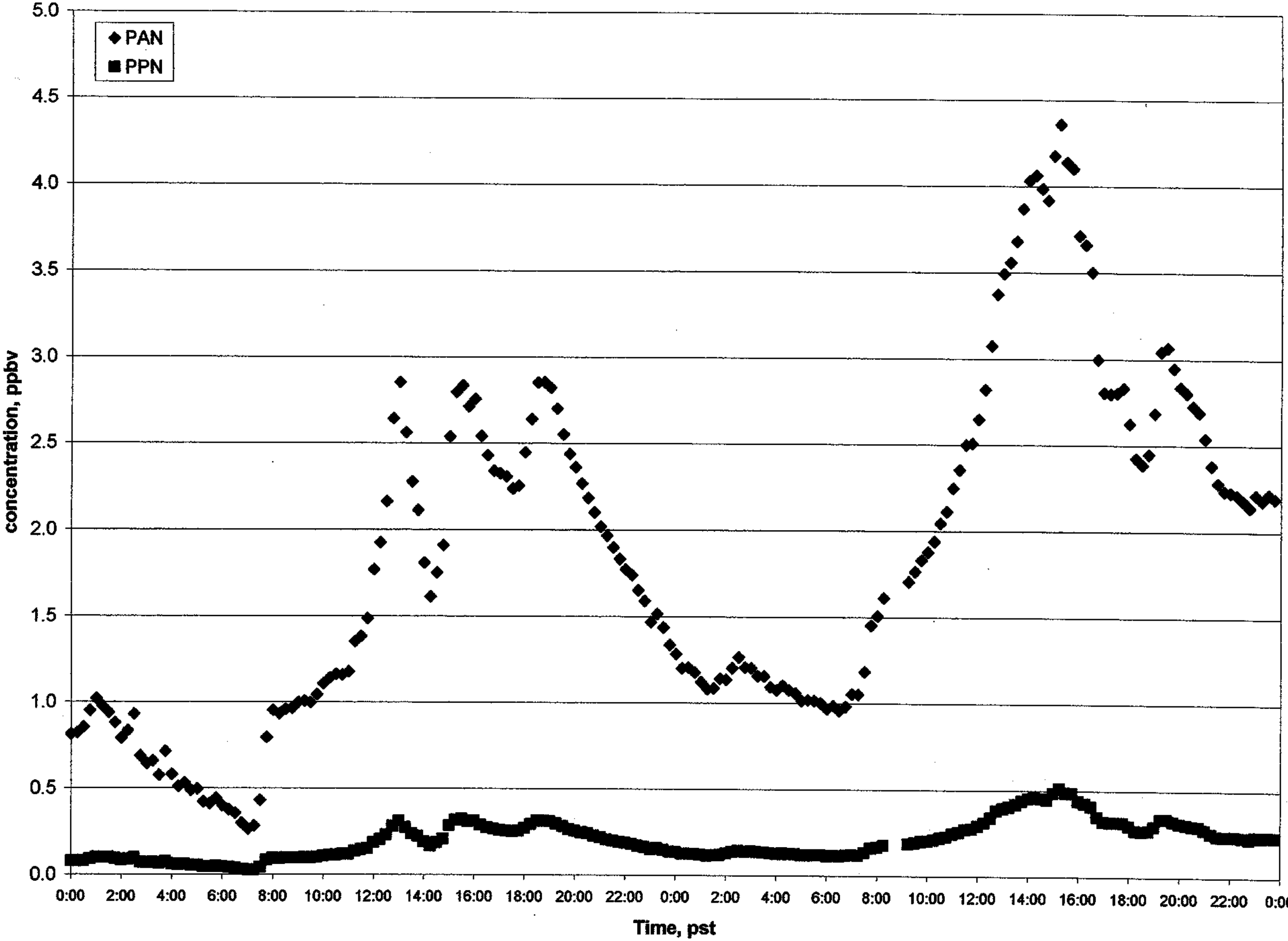

Figure 5.12 Ambient concentration of PAN, PPN and PCE, November 13, 2002

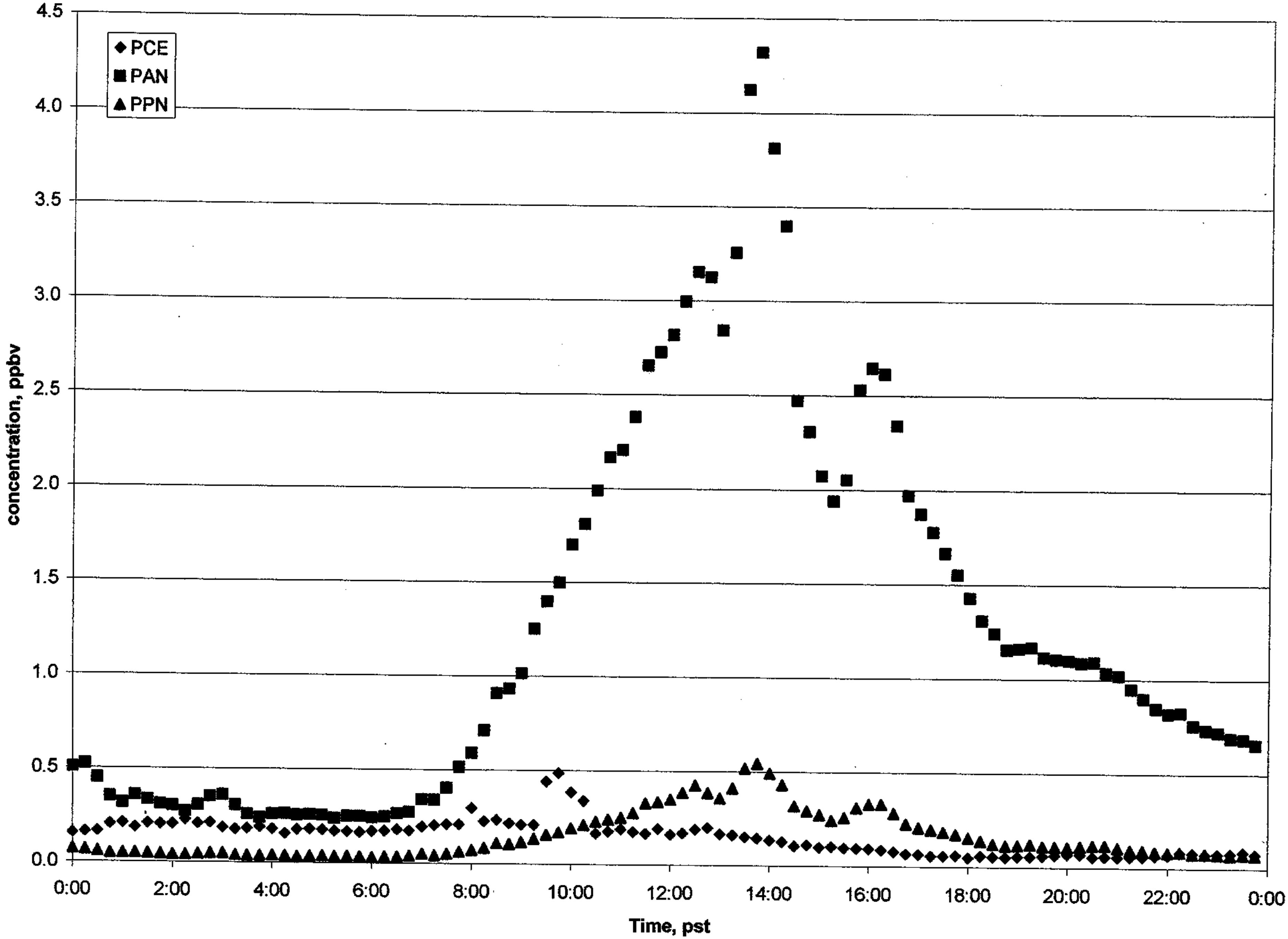

Figure 5.13 Composite diurnal profiles of PAN maxima for 2001, 2002 and 2003

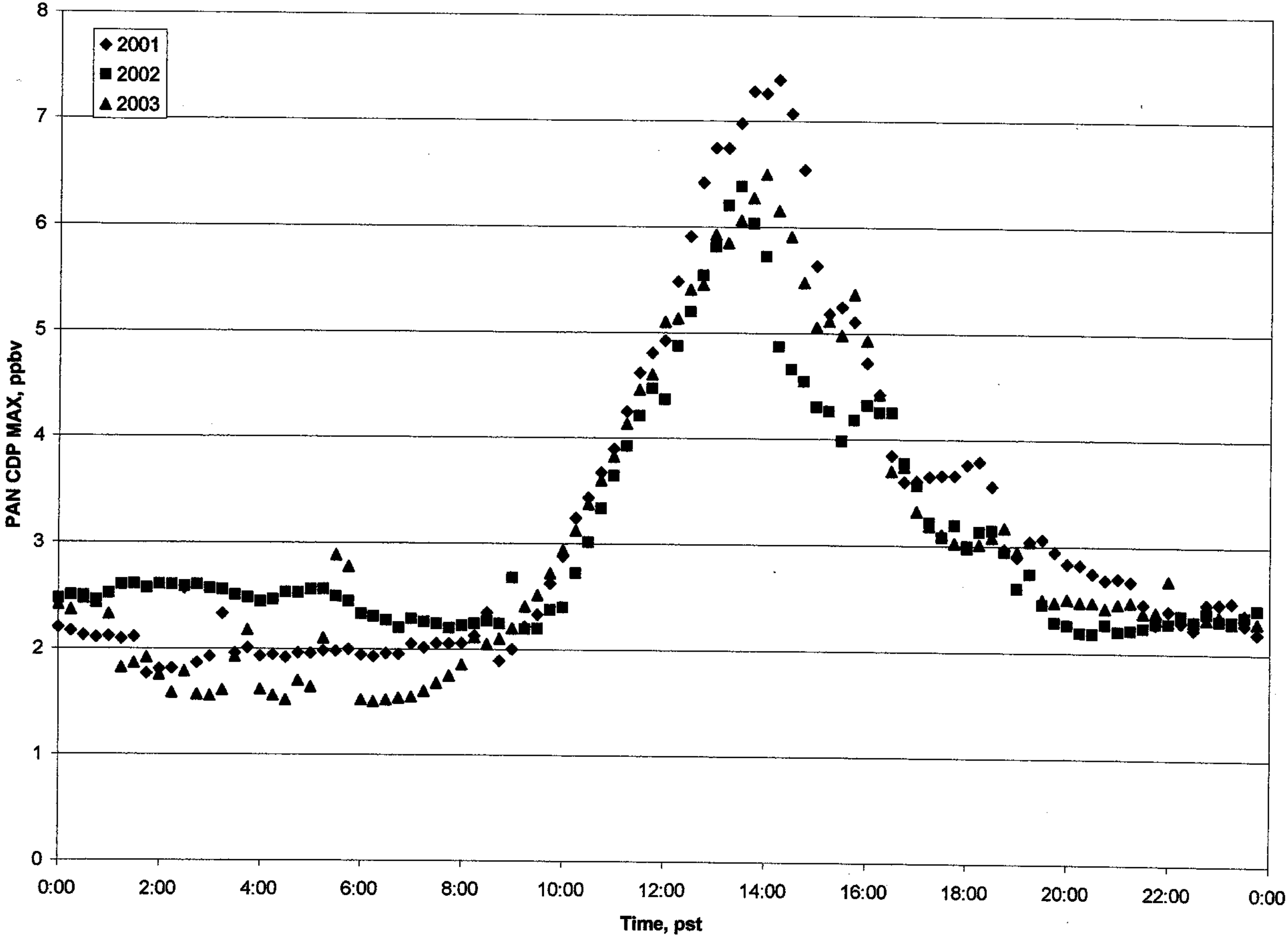

Figure 5.14 Ambient concentrations of PAN, PPN and PCE, November 27, 2001

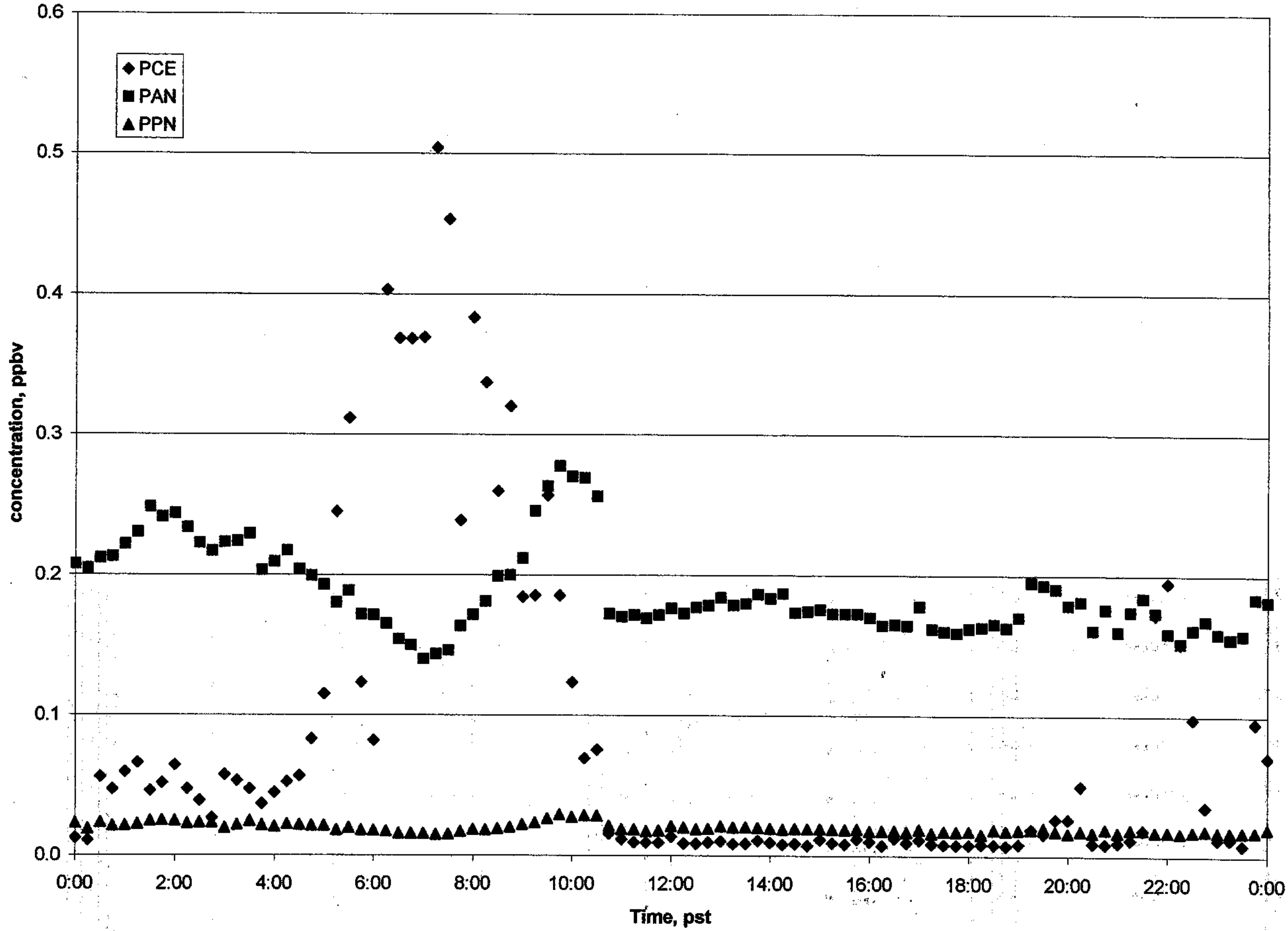

Figure 5.15 Ambient concentrations of PAN, PPN and PCE, December 29, 2001

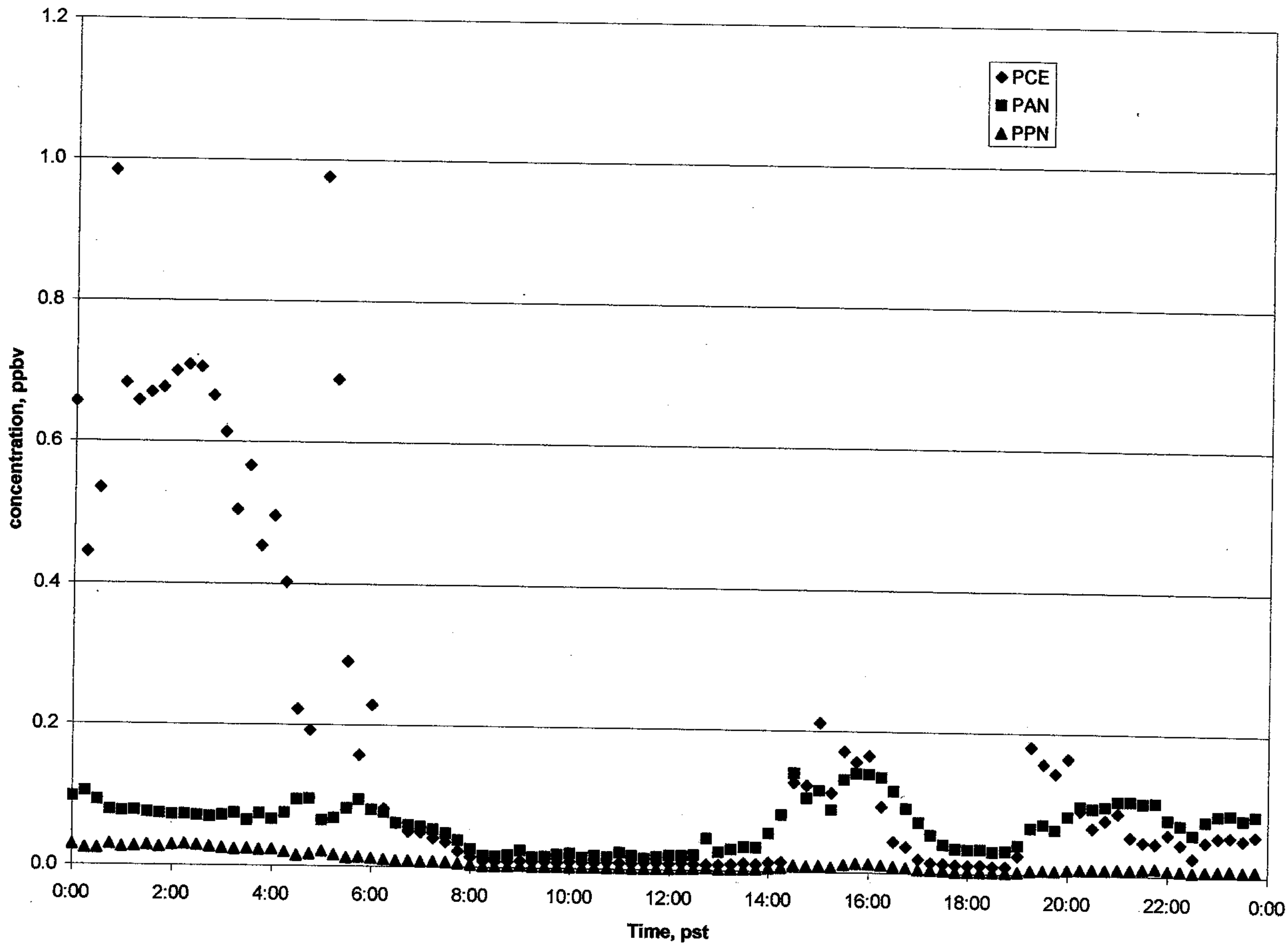

Figure 5.16 Ambient concentrations of PAN, PPN and PCE, December 25 – 26, 2001

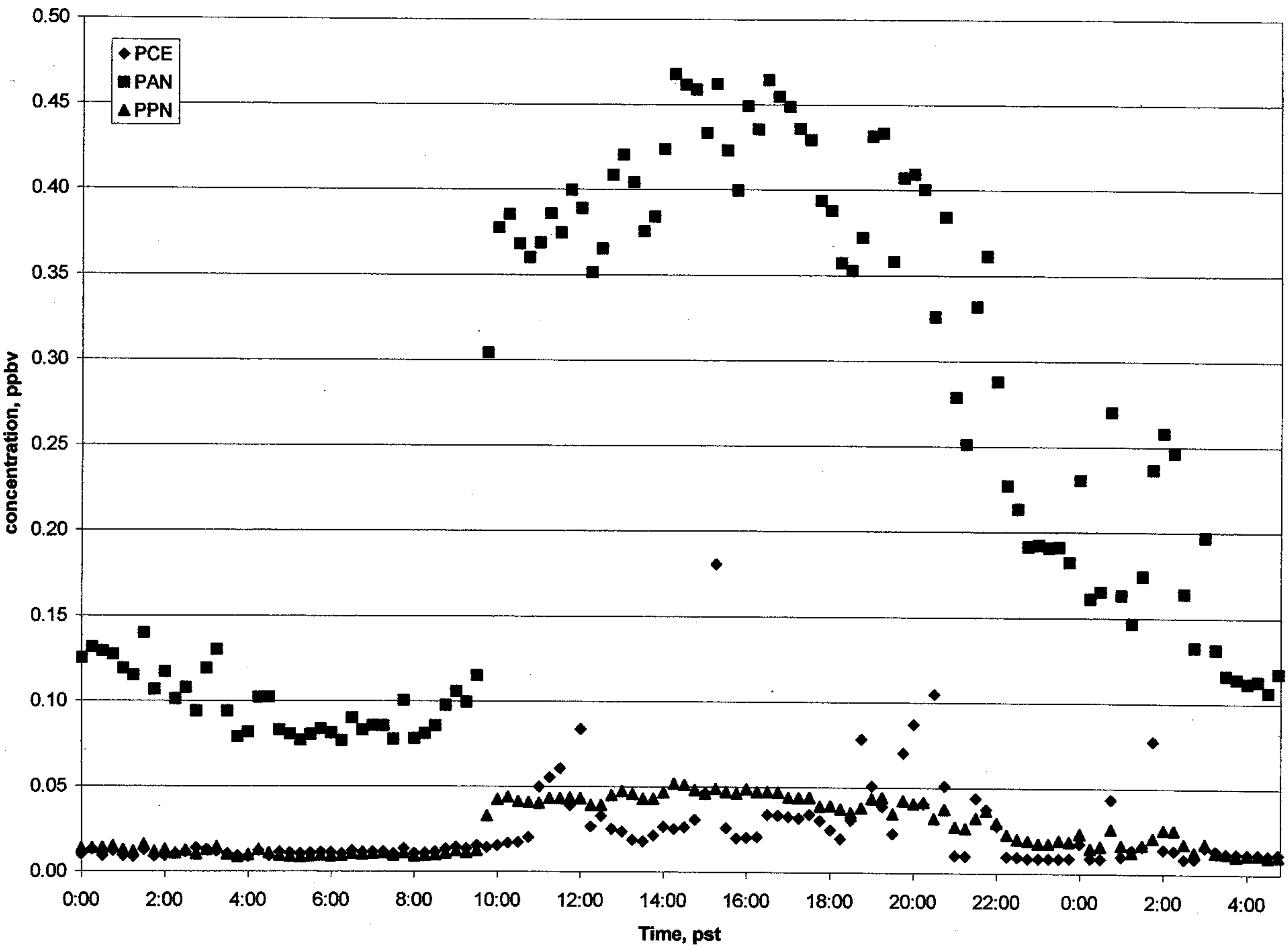

Figure 5.17 Ambient concentrations of PAN and PCE, November 25 – 28, 2002

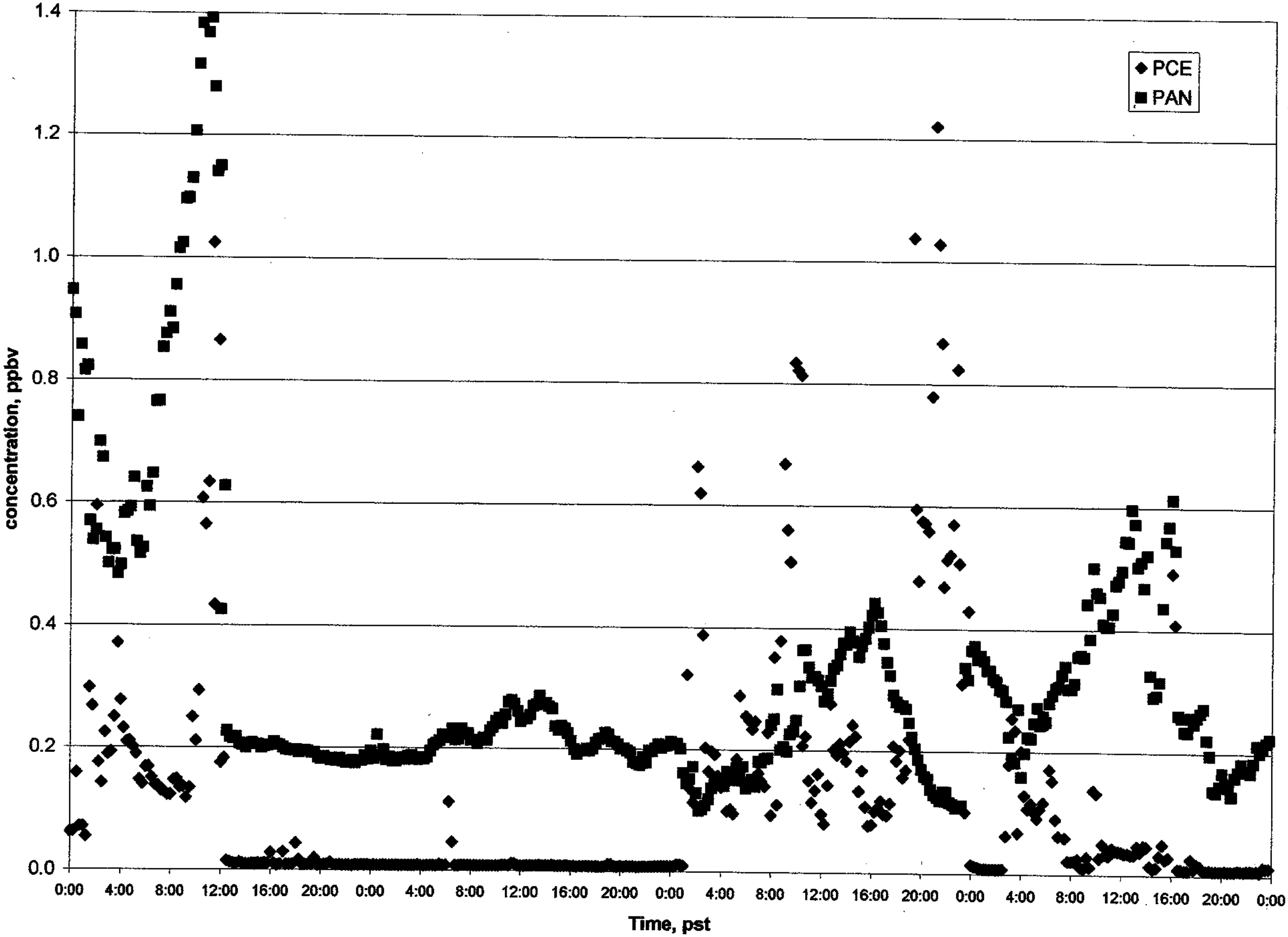

Figure 5.18 Ambient concentrations of PAN and PCE, December 22 – 23, 2002

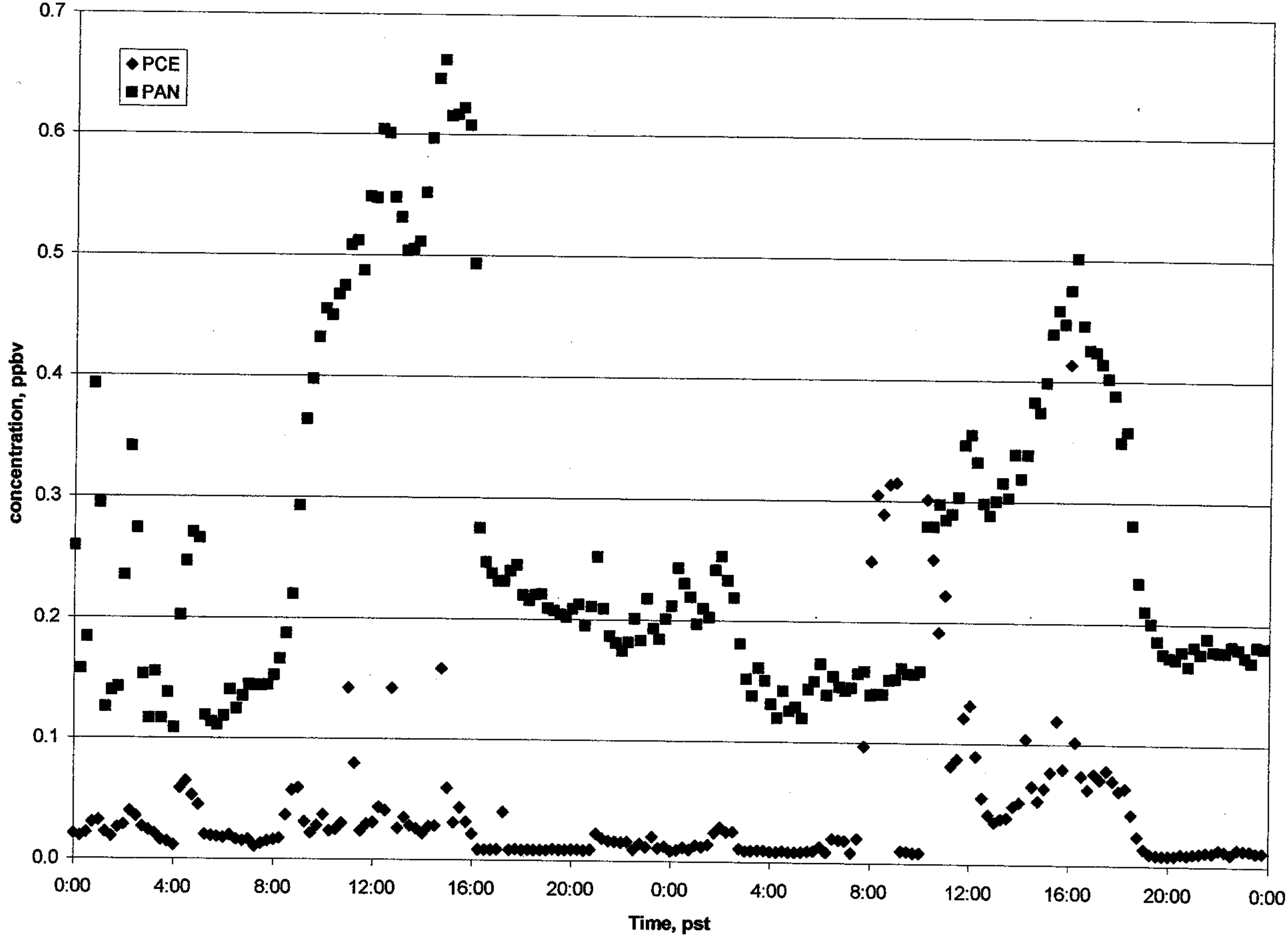

Figure 5.19 Ambient concentrations of PAN and PCE, January 5 –7, 2003

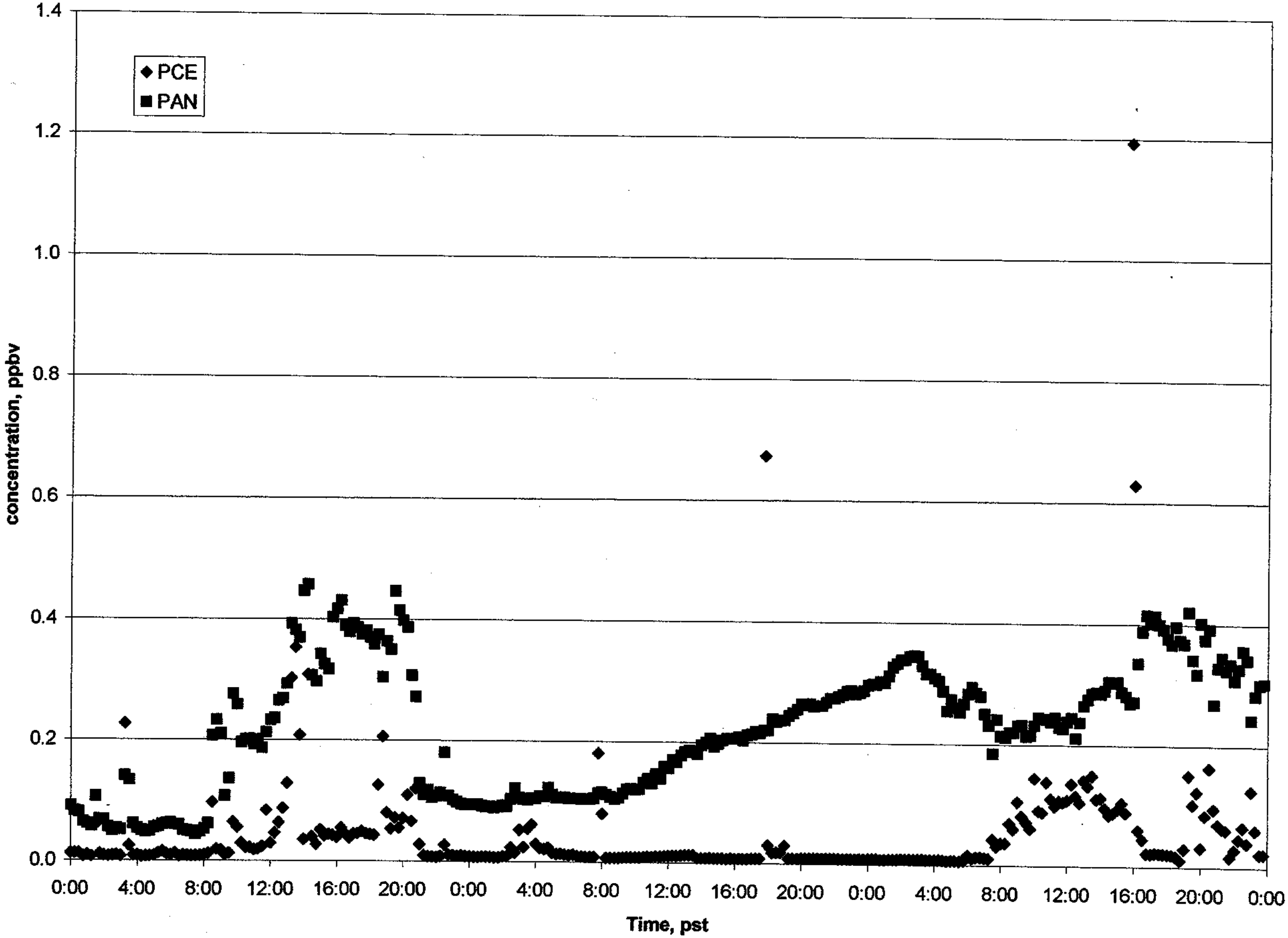

Figure 5.20 Ambient concentrations of PAN, PPN and PCE, October 15 – 17, 2002

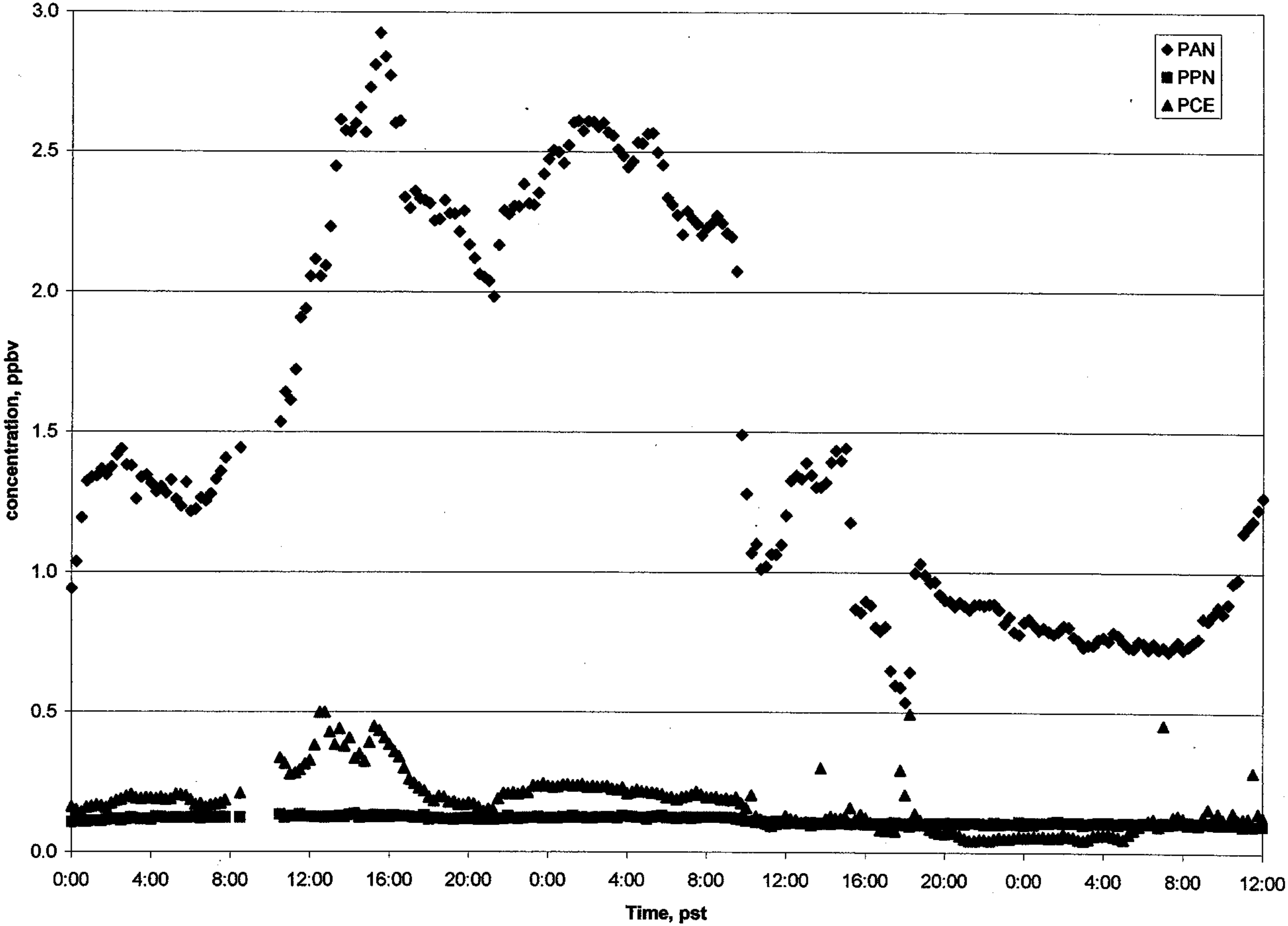

Figure 6.1 Scatterplot of log PPN vs. log PAN for all 2001 data

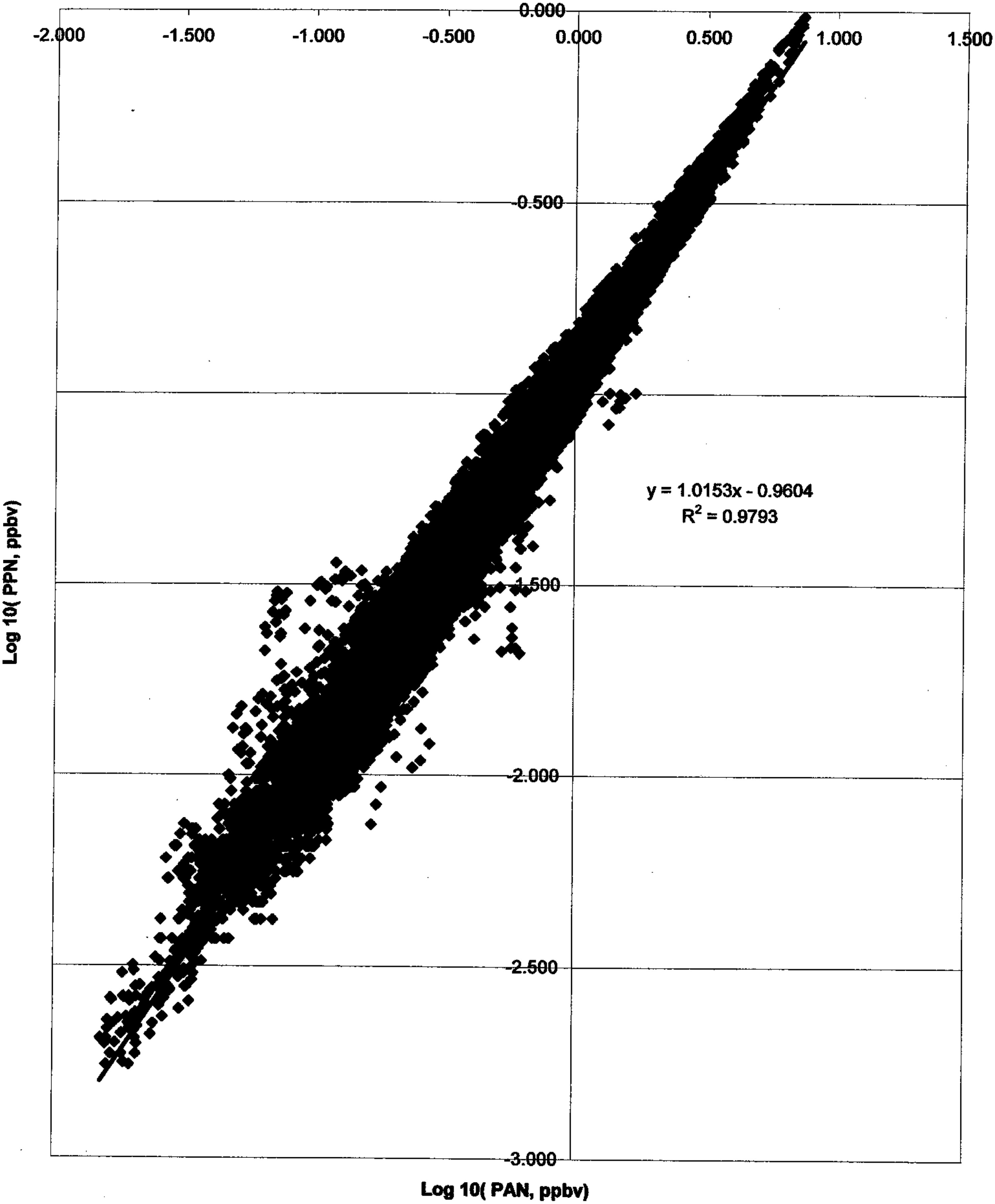

Figure 6.2 Scatterplot of log PPN vs. log PAN for all 2002 data

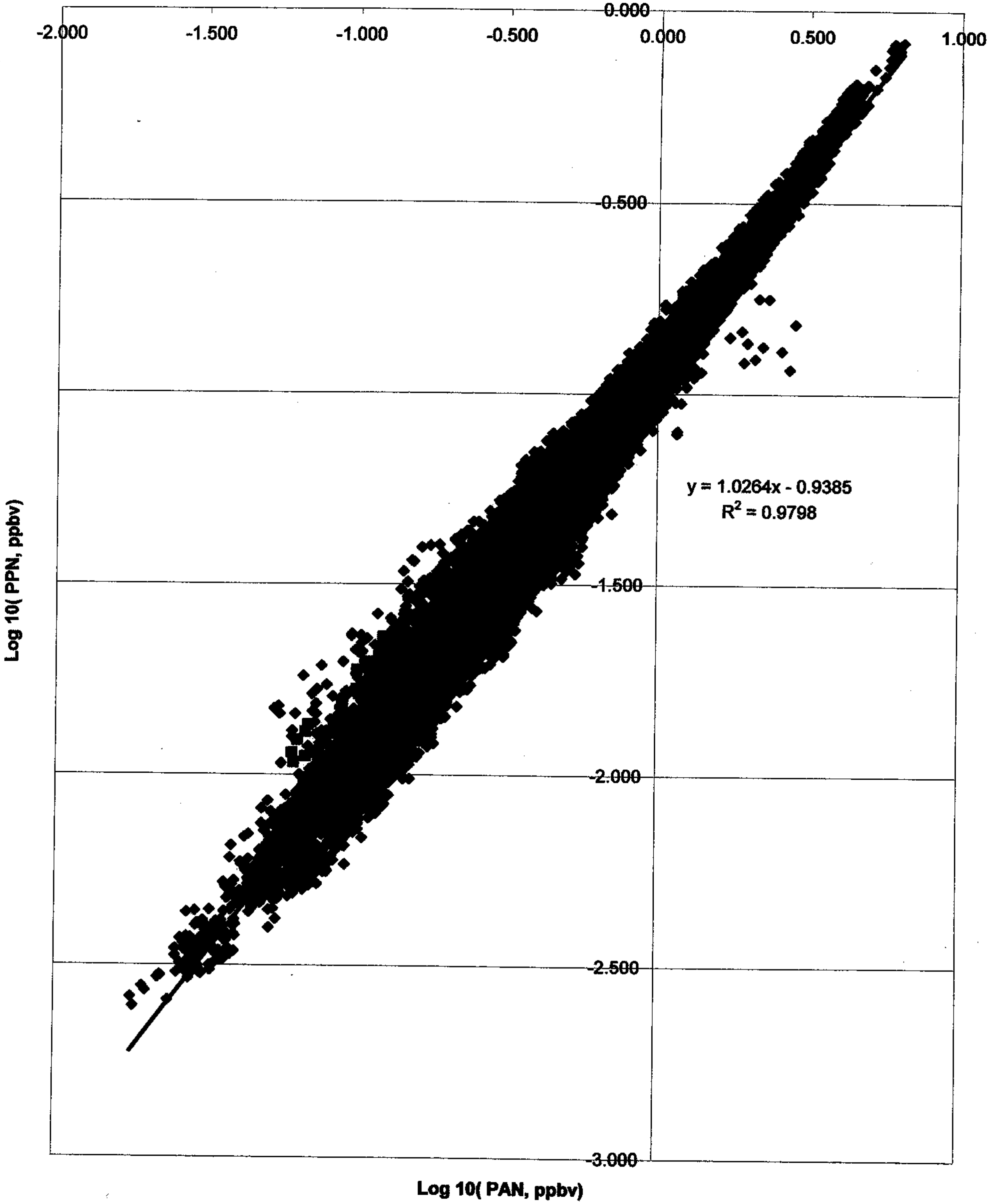

Figure 6.3 Scatterplot of log PPN vs. log PAN for all 2003 data

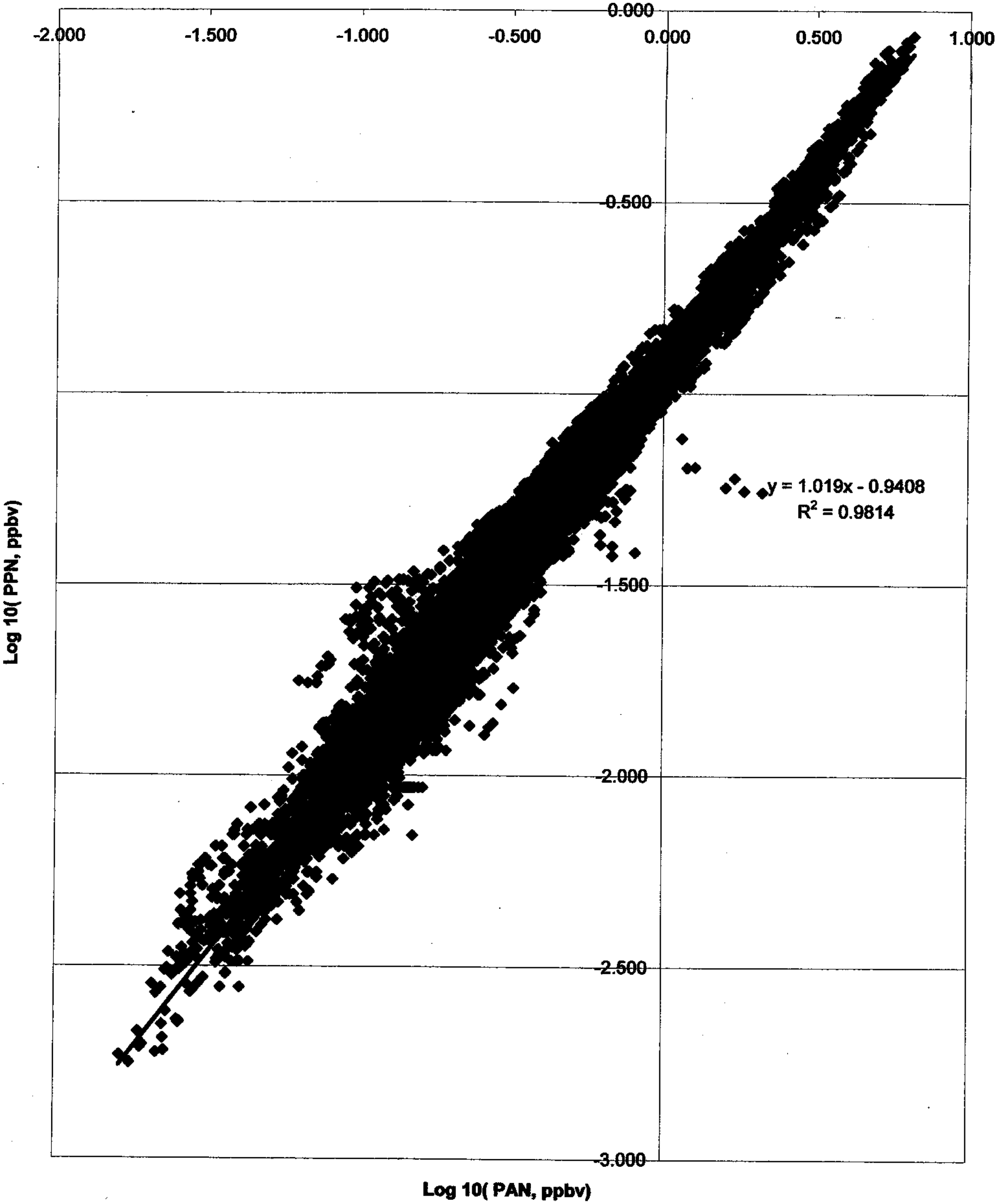

Figure 6.4 Histogram of PPN/PAN concentration ratios, all 2001 data

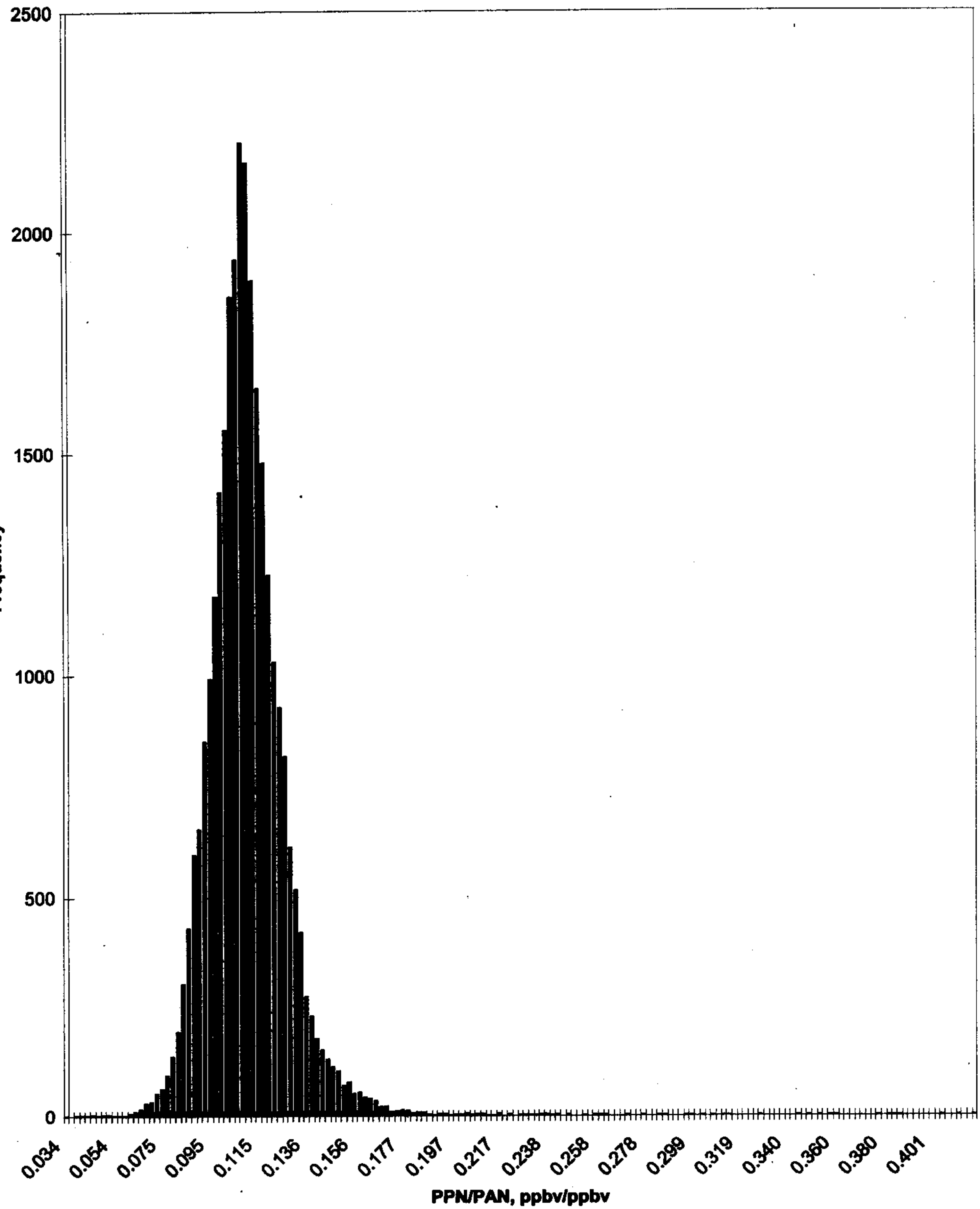

Figure 6.5 Histogram of PPN/PAN concentration ratios, all 2002 data

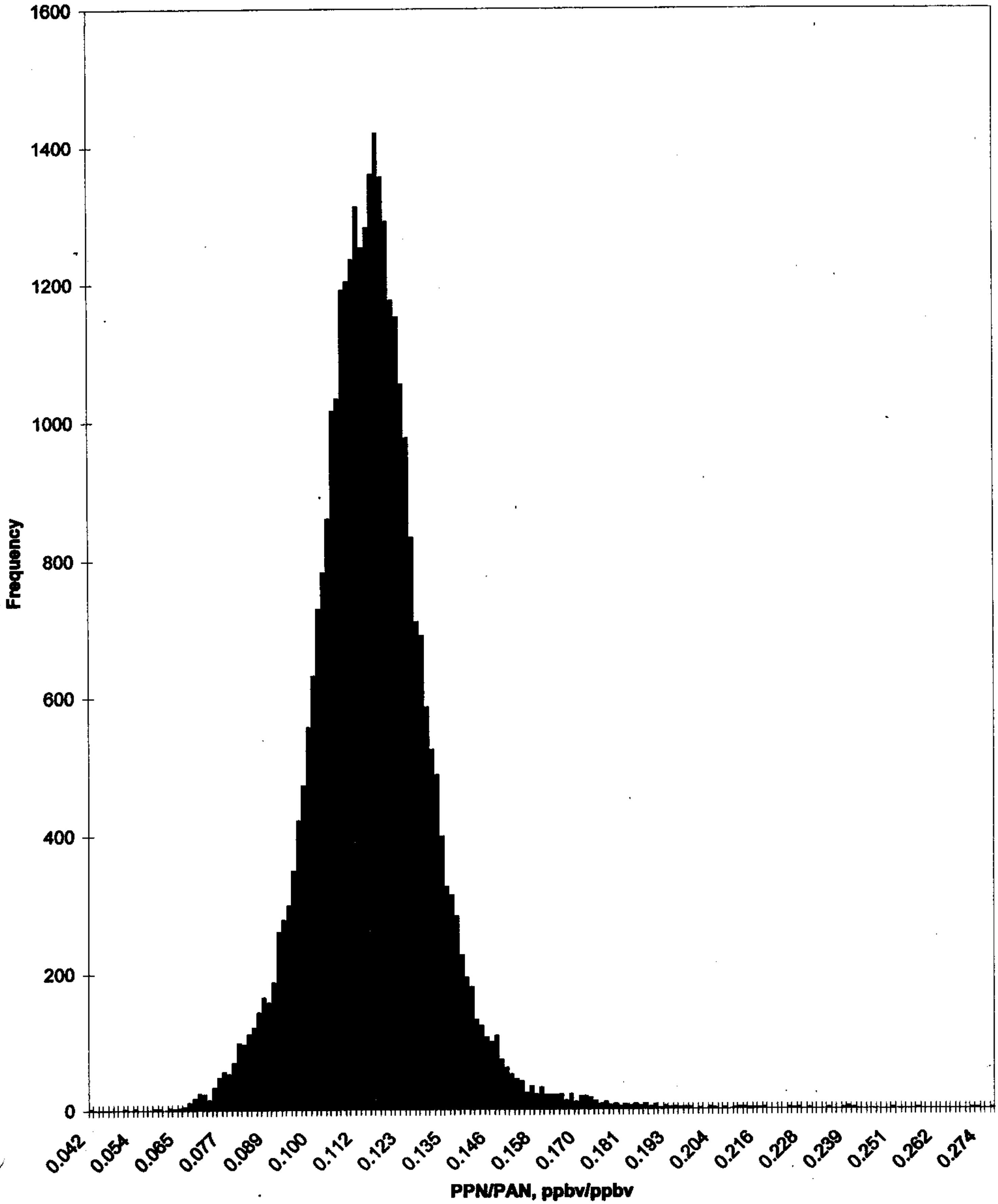

Figure 6.6 Histogram of PPN/PAN concentration ratios, all 2003 data

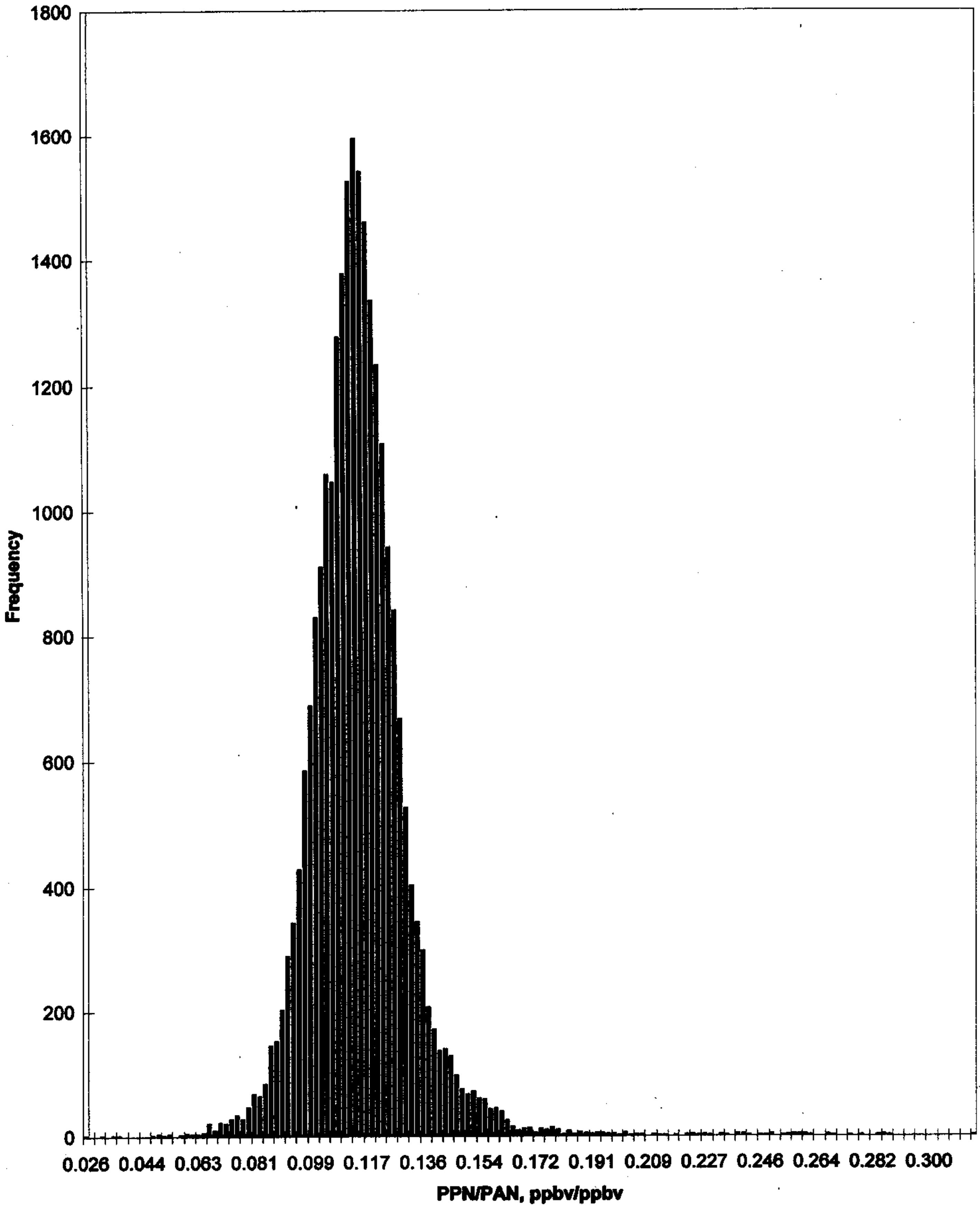

Figure 6.7 Scatterplot of monthly-averaged concentrations of PPN vs. those of PAN

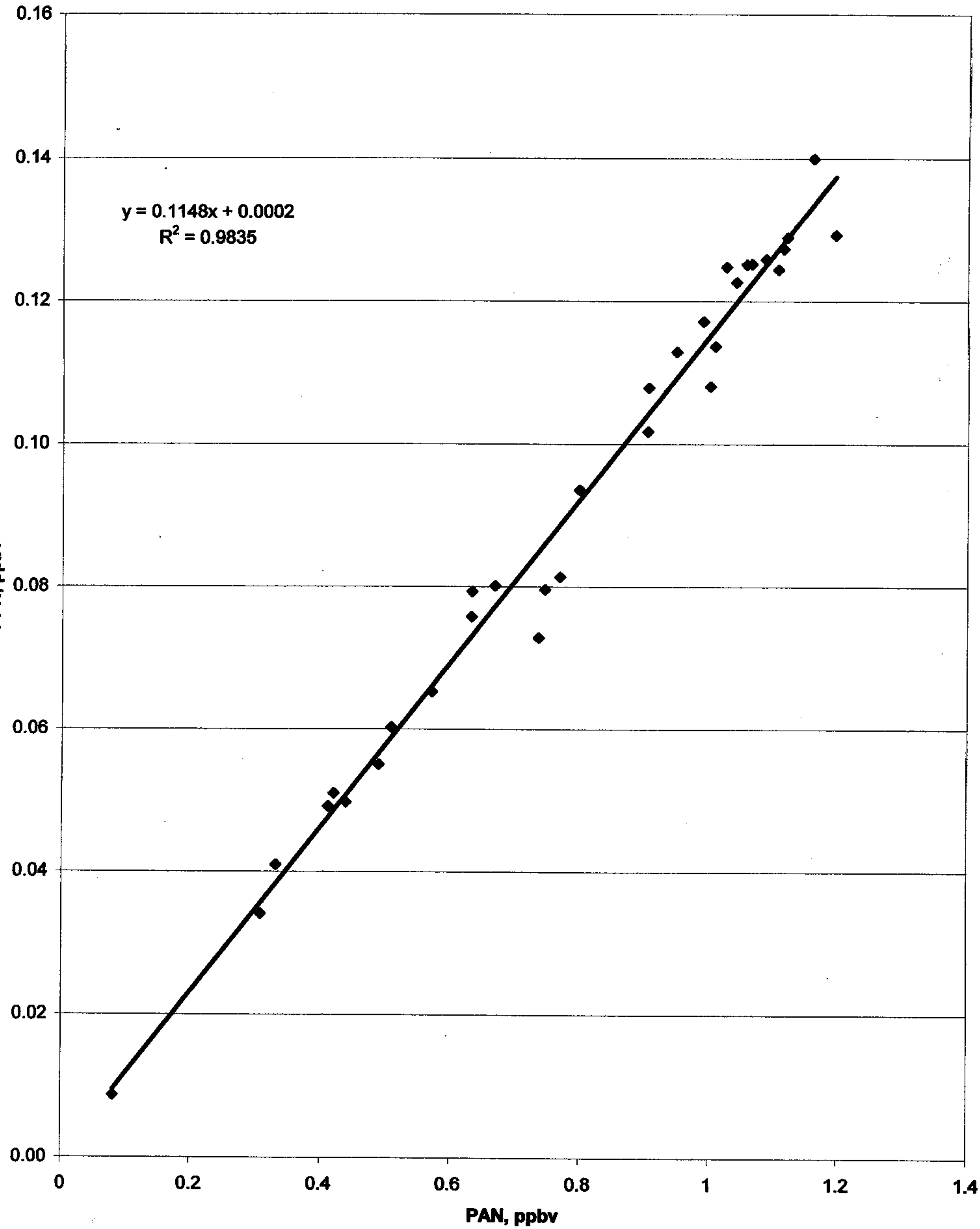

Figure 6.8 Scatterplot of monthly-averaged PPN/PAN concentration ratios vs. monthly averaged PAN concentrations

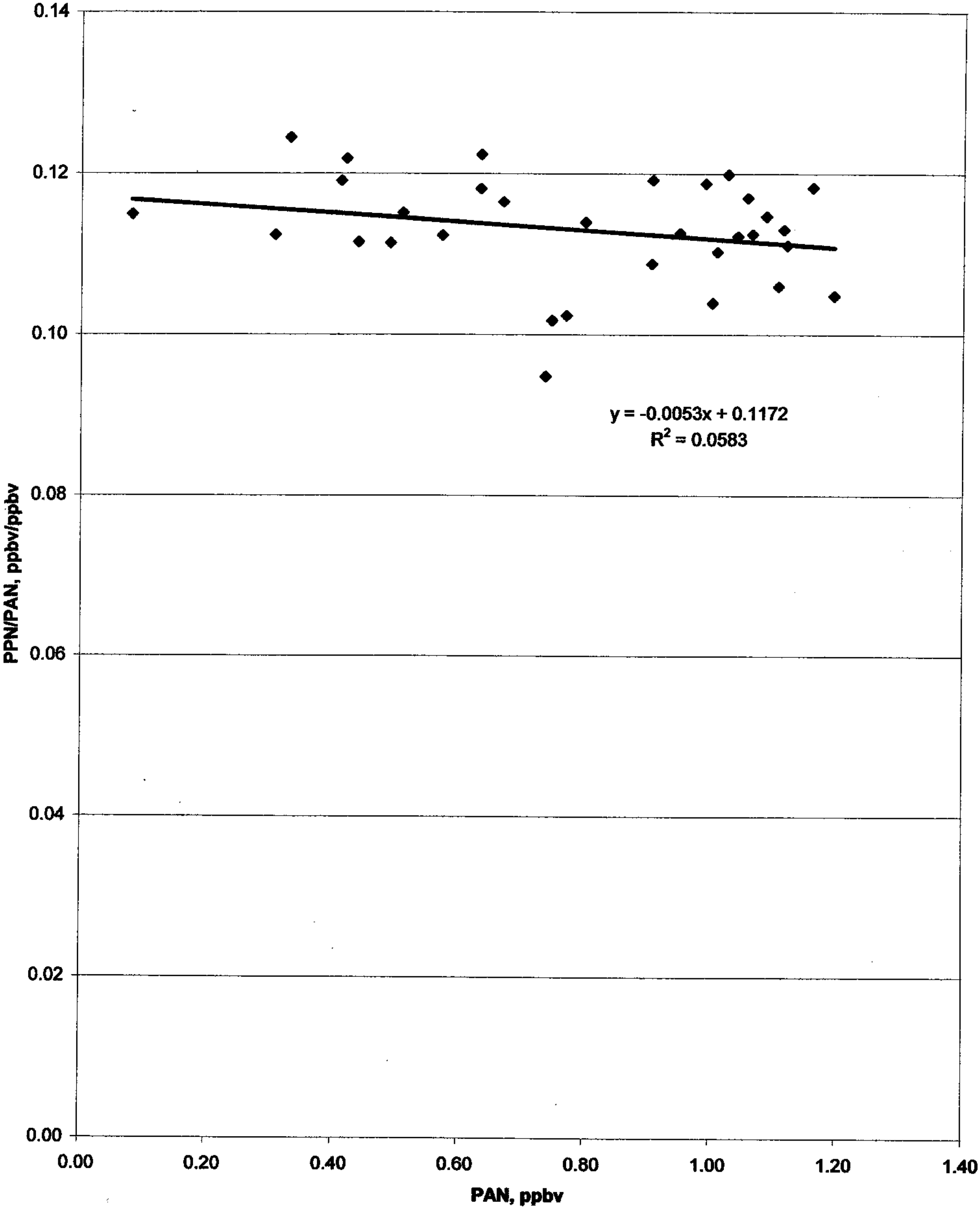

Figure 6.9 Time series plot of the slopes calculated from regression analysis of PPN vs. PAN for each month

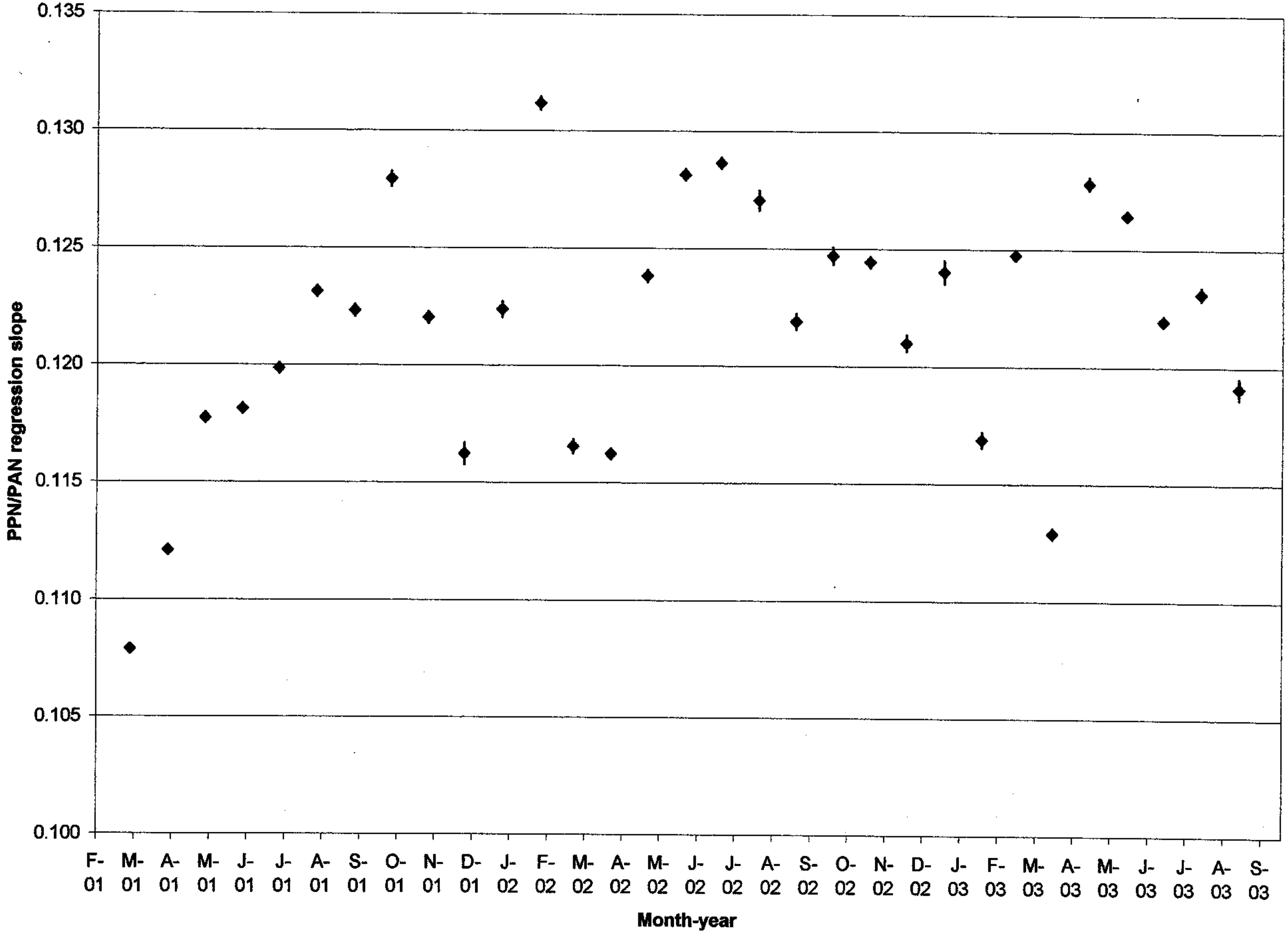

Figure 6.10 Time series plot of the intercepts calculated from regression analysis of PAN vs. PPN for each month

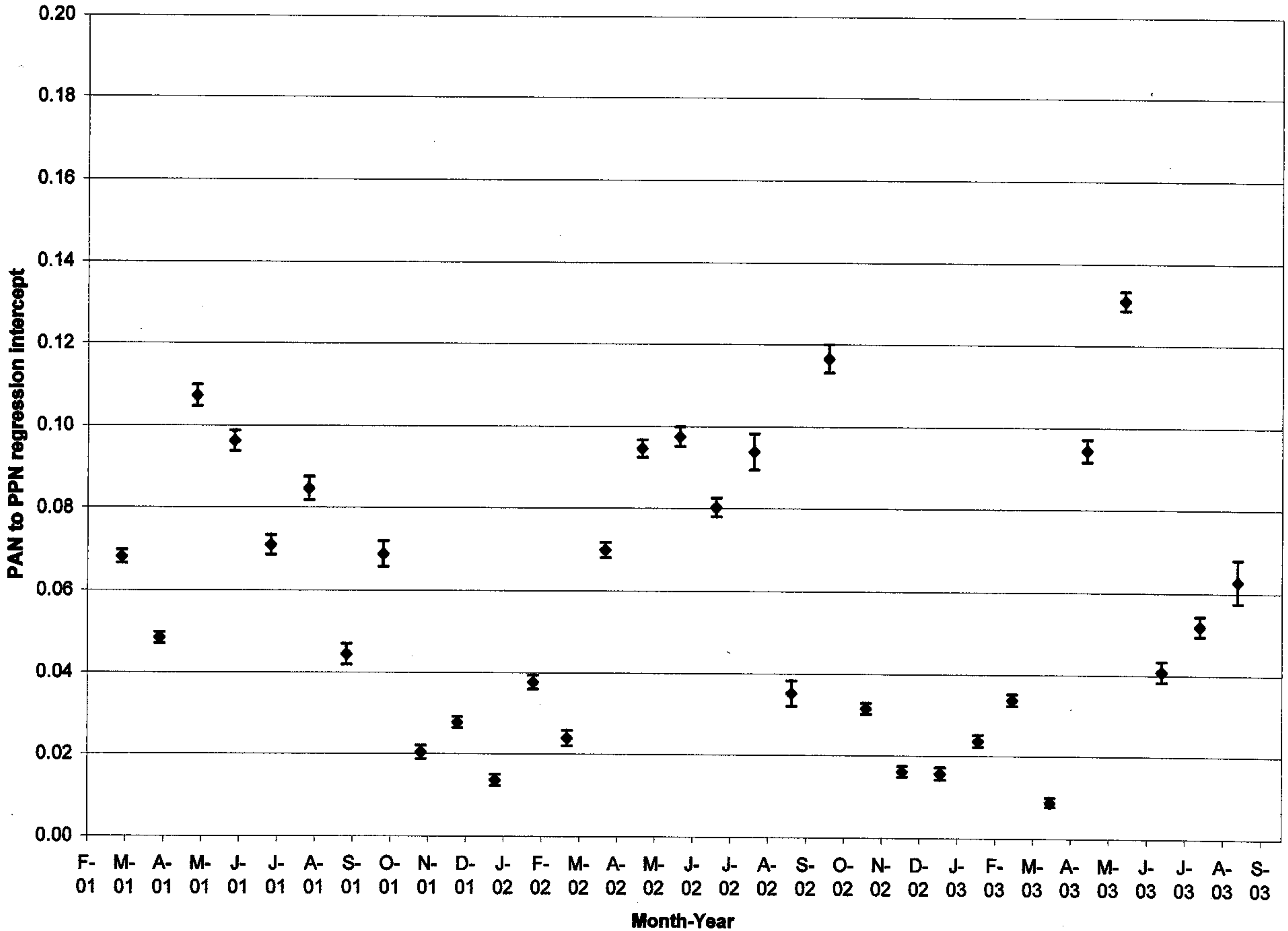

Figure 6.11 Composite diurnal profile of study-averaged PPN/PAN concentration ratios shown with standard deviations

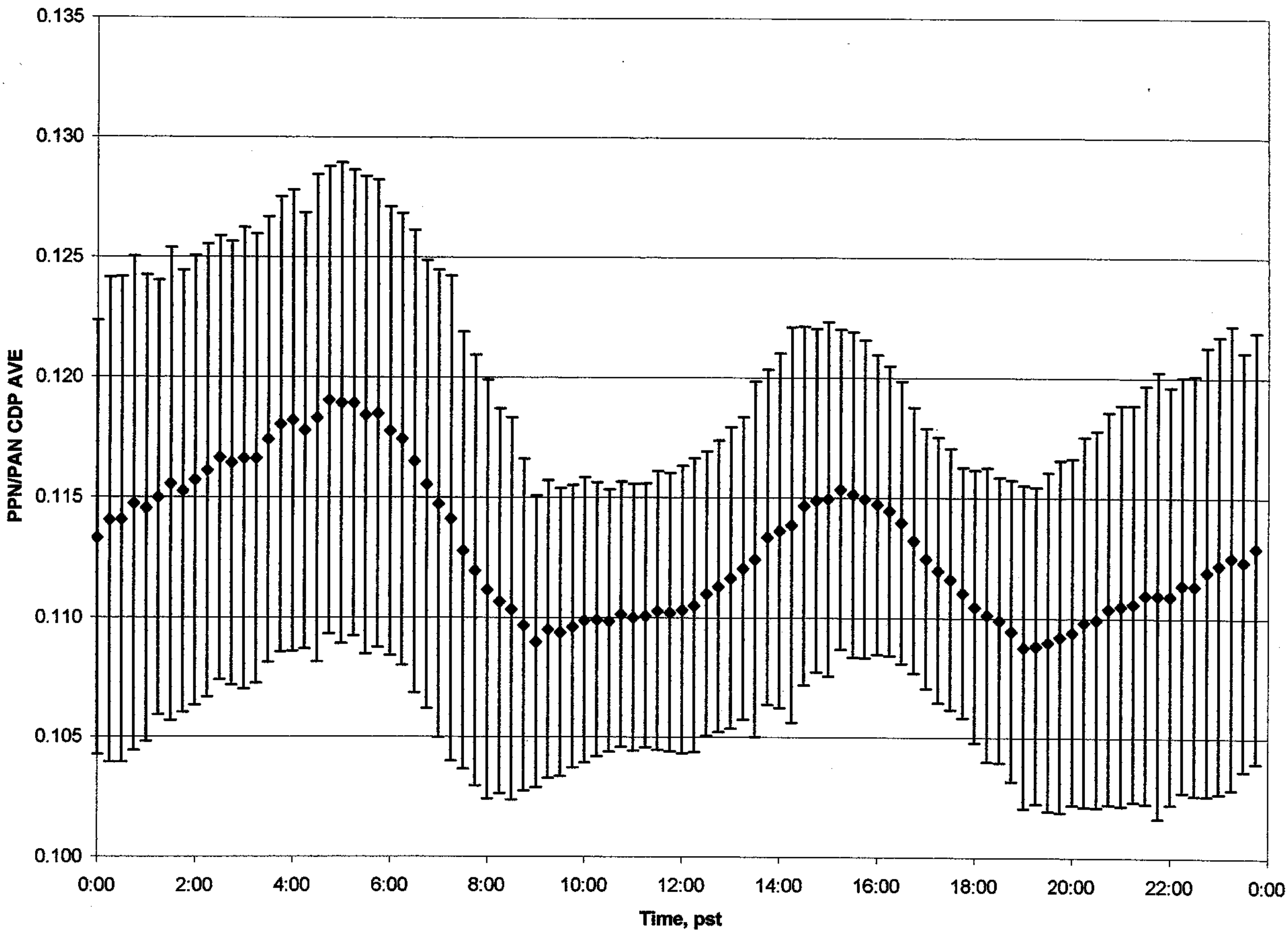

Figure 6.12 Composite diurnal profile of PPN/PAN concentration ratios, 2001

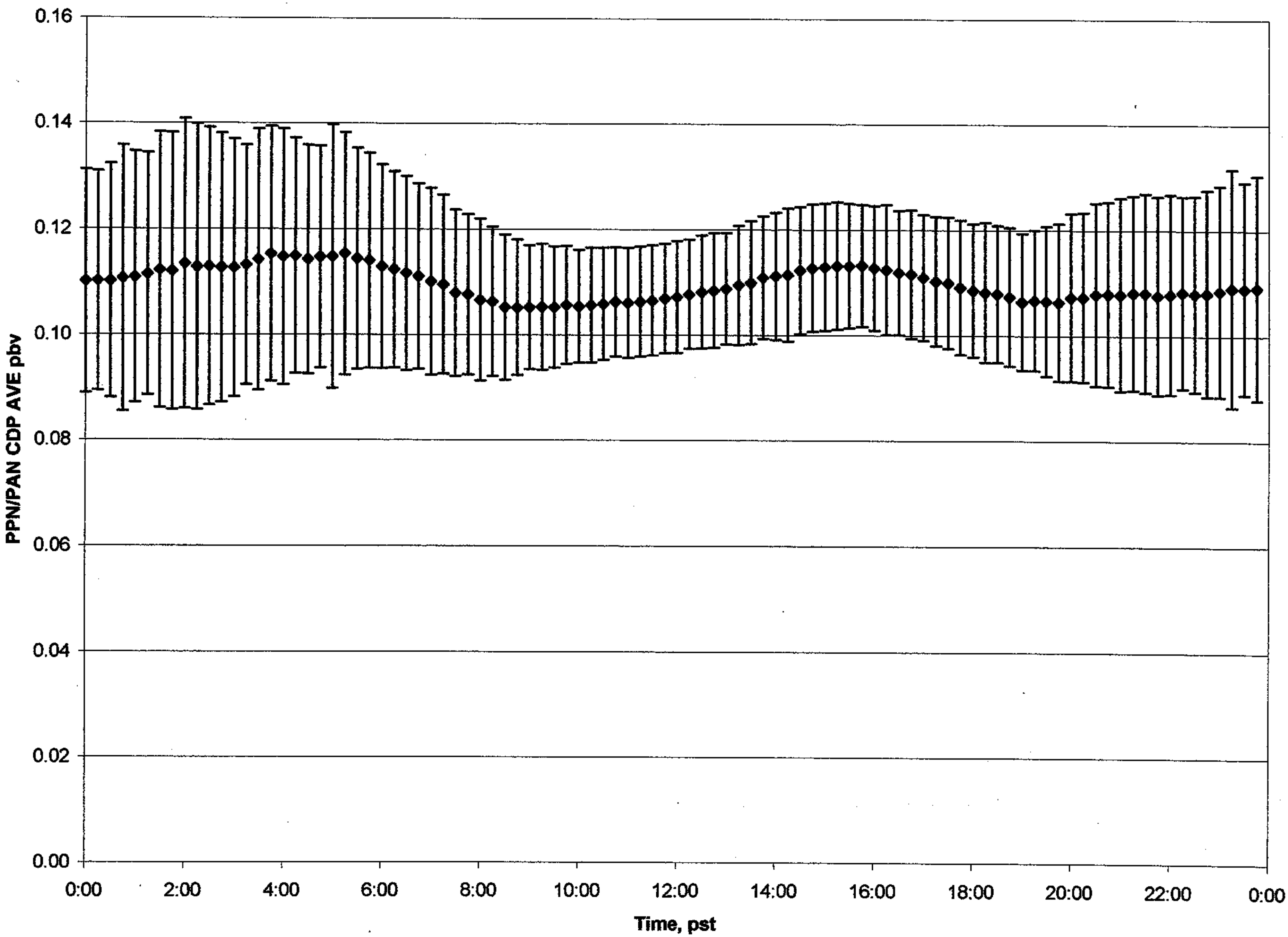

Figure 6.13 Composite diurnal profile of PPN/PAN concentration ratios, 2002

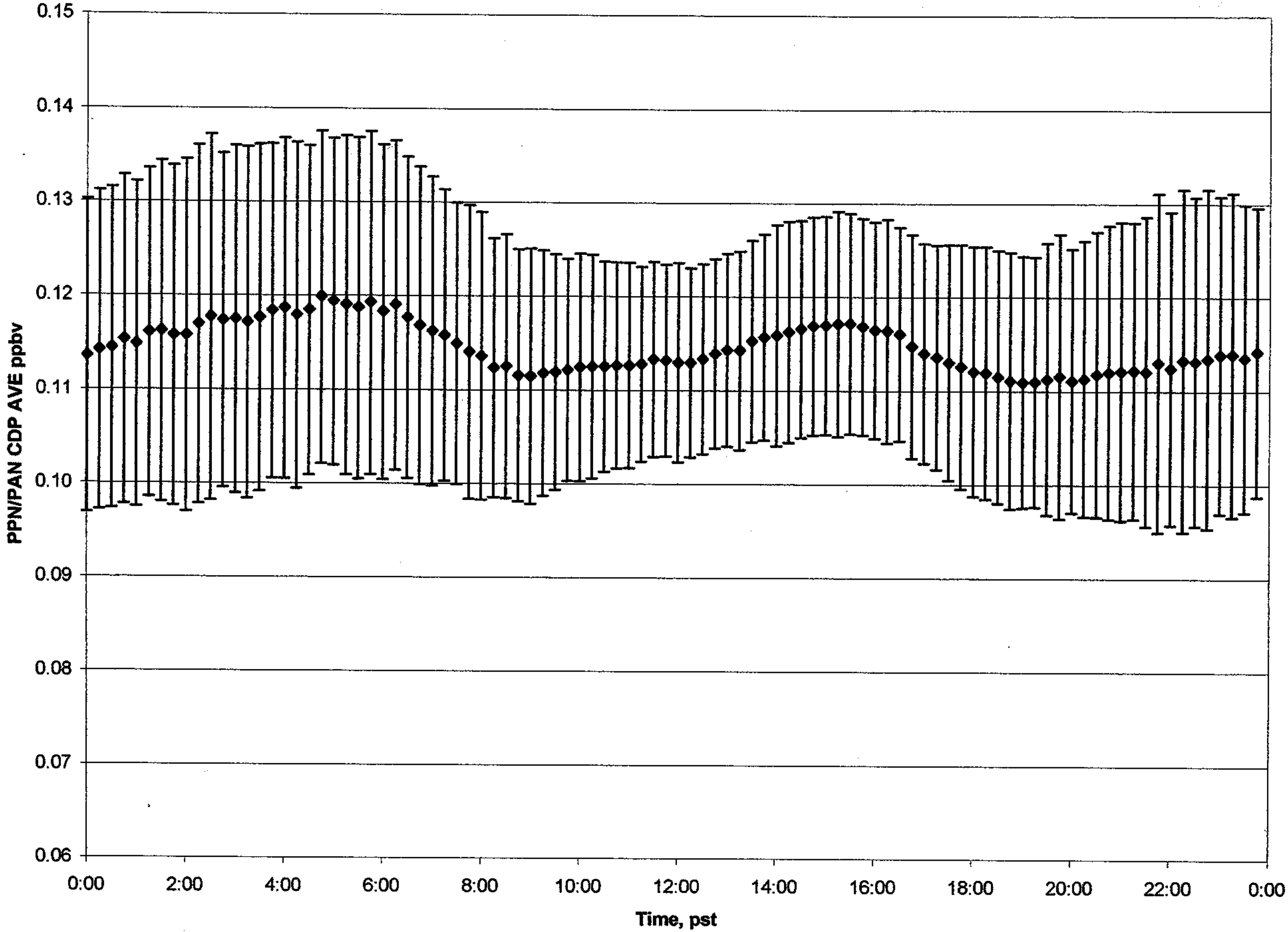

Figure 6.14 Composite diurnal profile of PPN/PAN concentration ratios, 2003

Figure 6.15 Comparison of the PPN/PAN concentration ratio composite diurnal profiles for 2001, 2002 and 2003

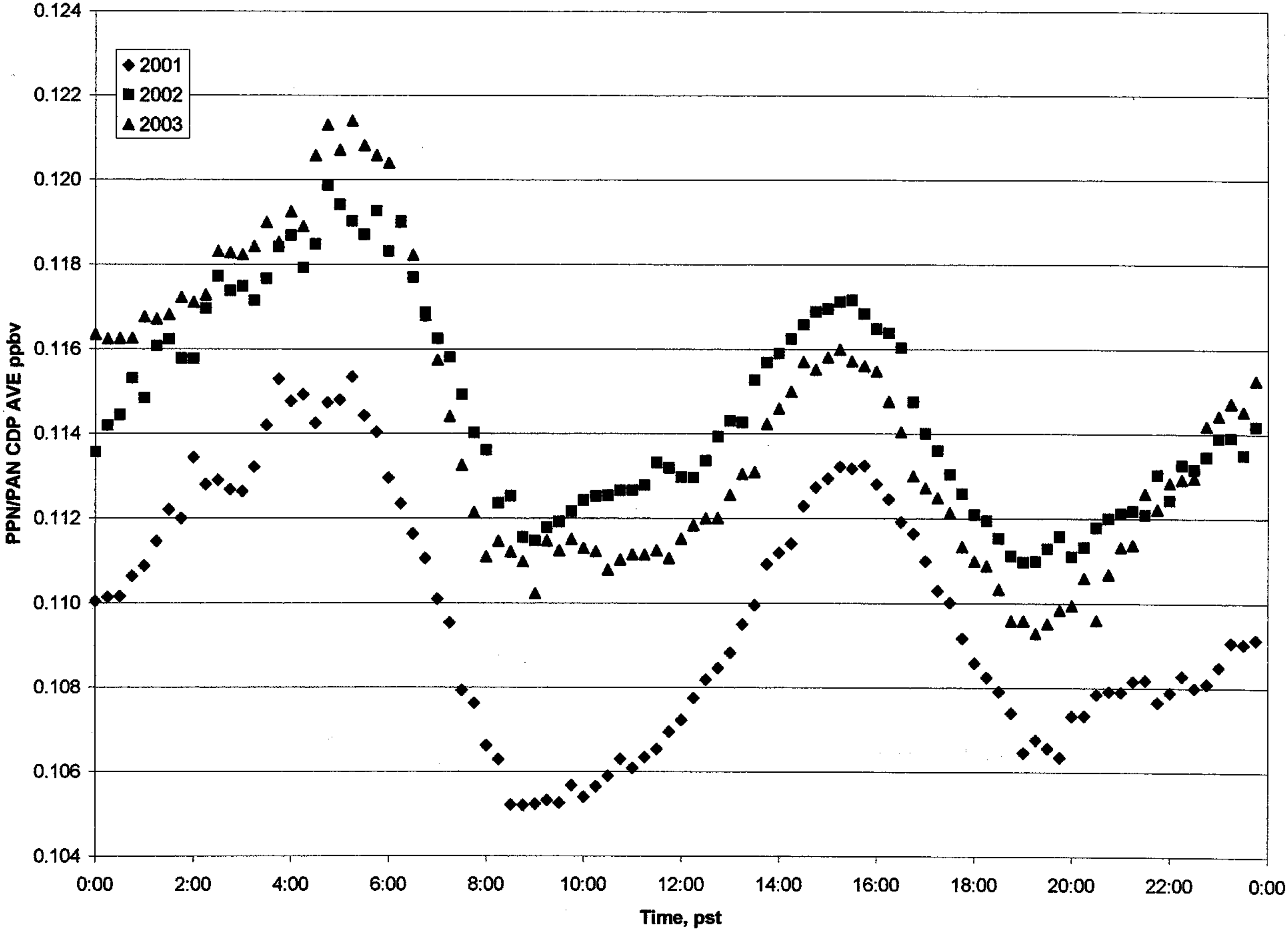

Figure 6.16 Monthly-averaged CDP of the PPN/PAN concentration ratios, 2001

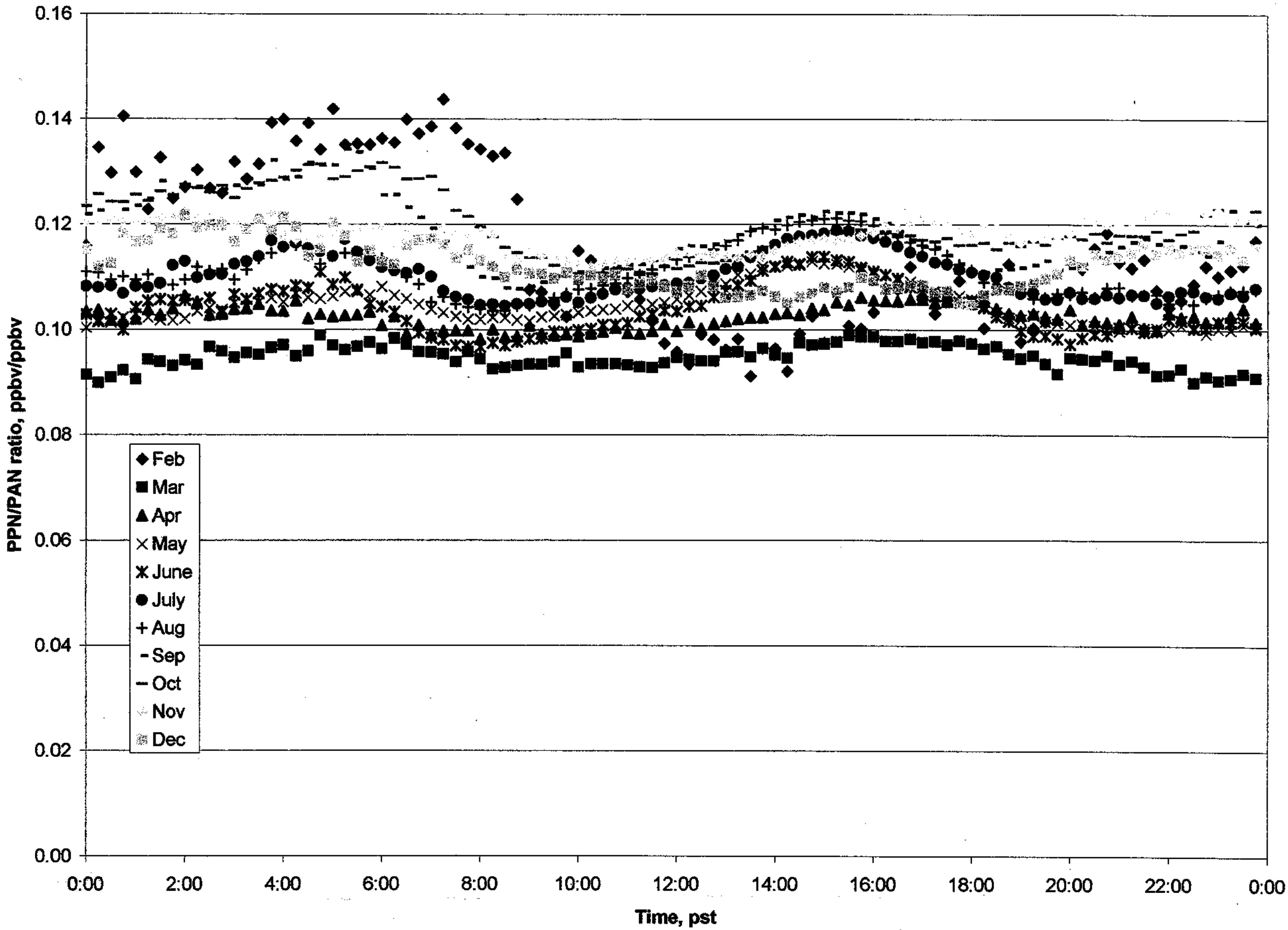

Figure 6.17 Monthly-averaged CDP of the PPN/PAN concentration ratios, 2002

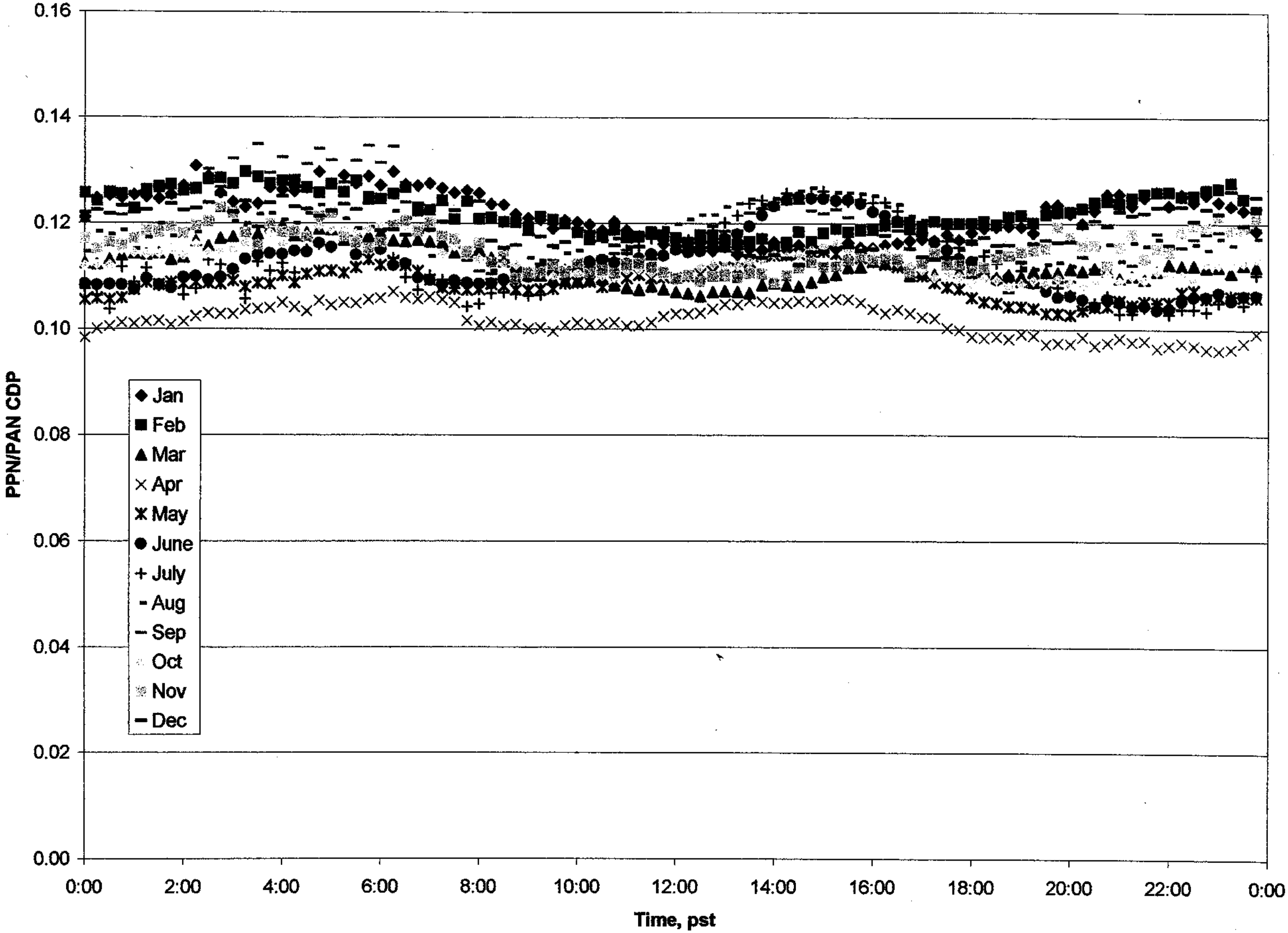

Figure 6.18 Monthly-averaged CDP of the PPN/PAN concentration ratios, 2003

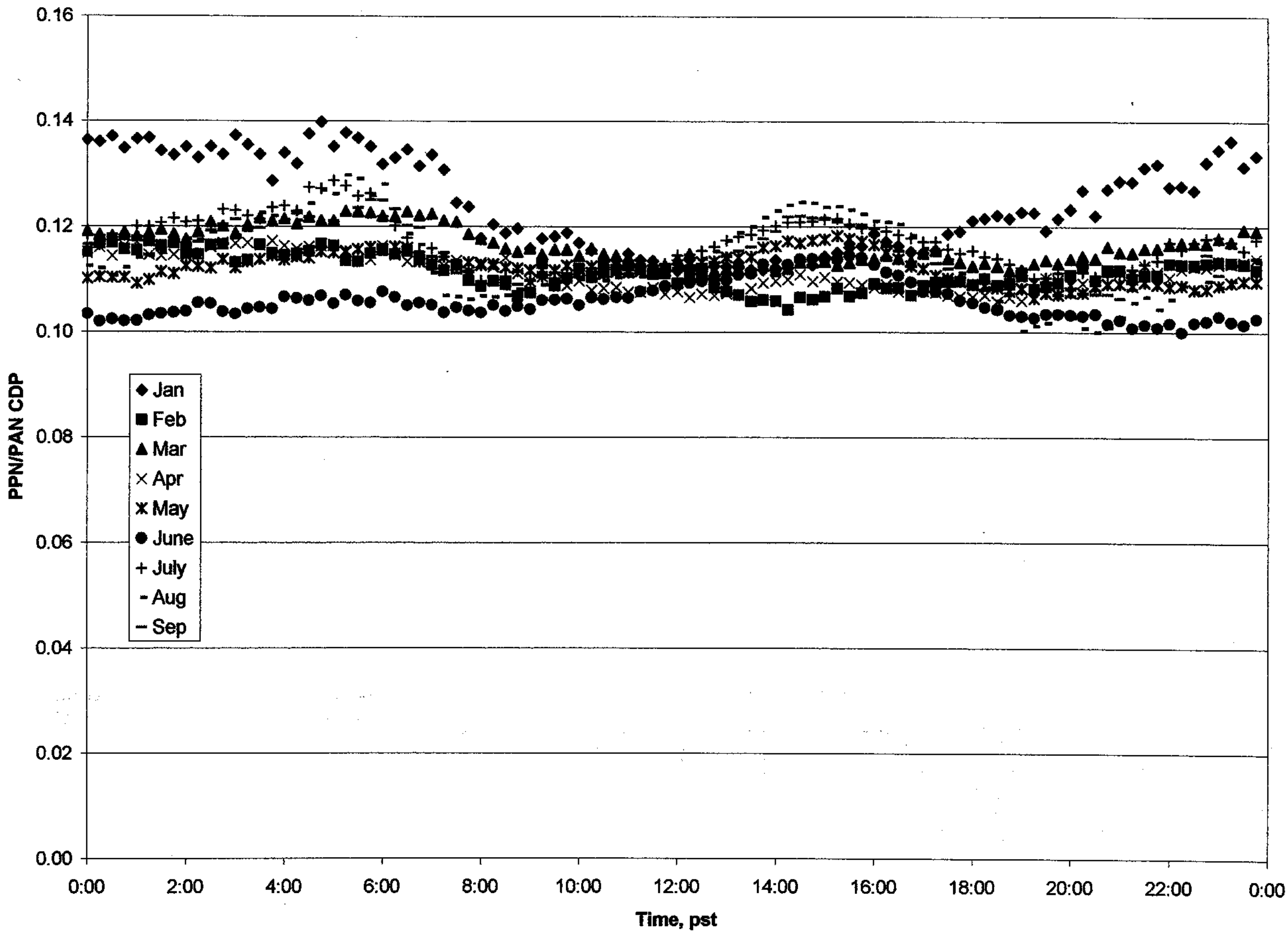

Figure 6.19 Monthly-averaged CDP of the PPN/PAN concentration ratios, July, August and September 2001

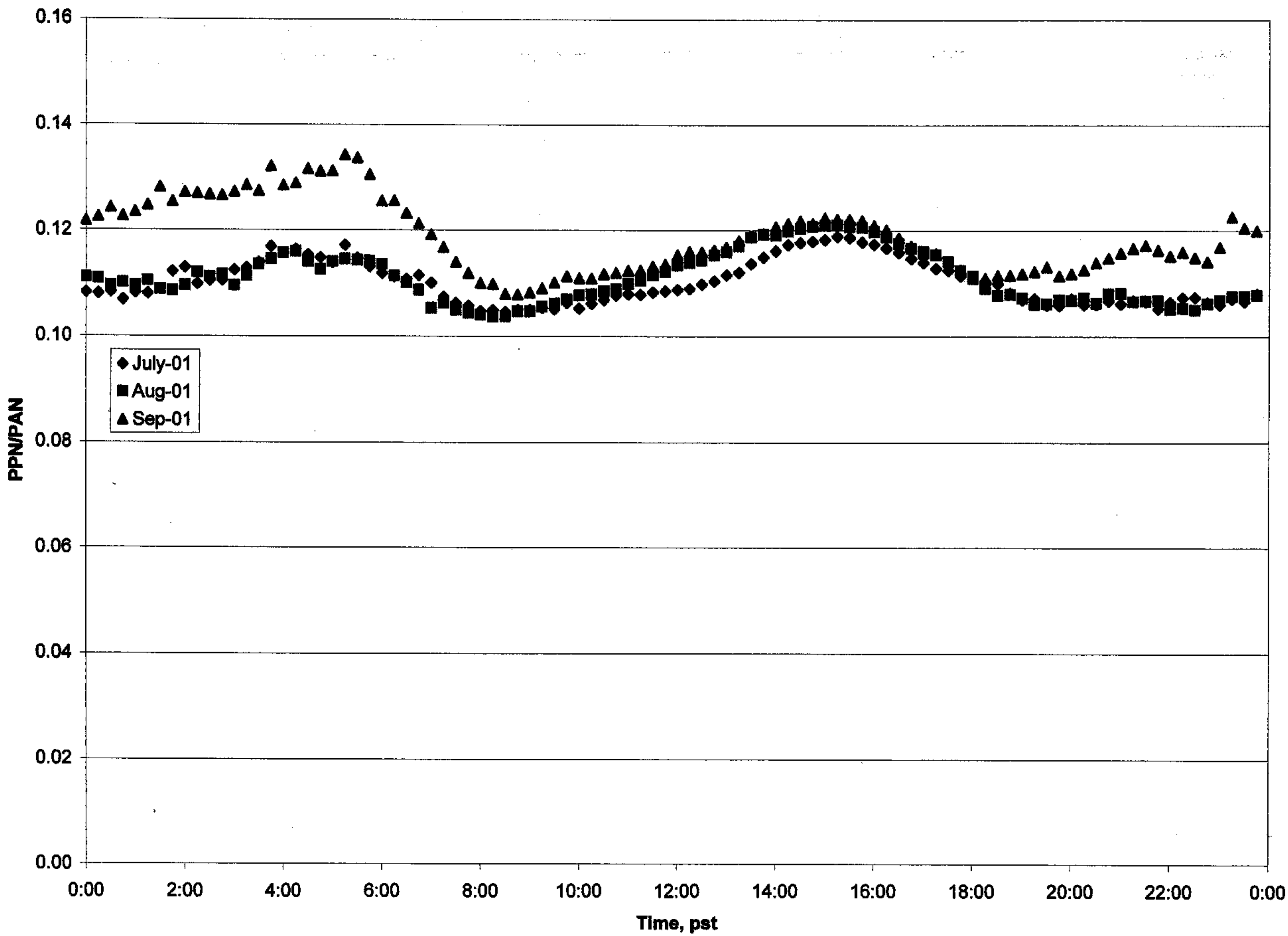

Figure 6.20 Monthly-averaged CDP of the PPN/PAN concentration ratios, June – September 2002

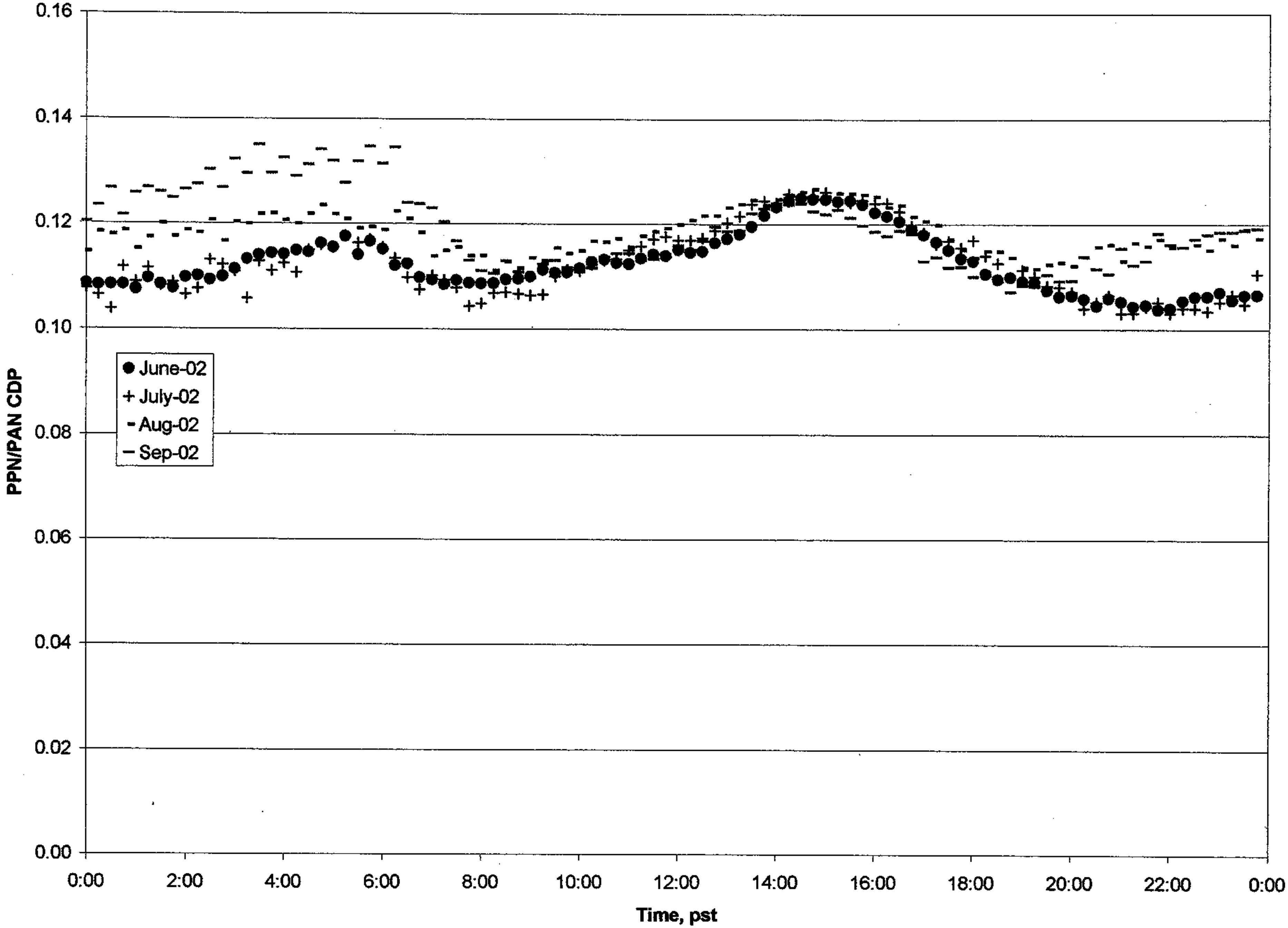

Figure 6.21 Monthly-averaged CDP of the PPN/PAN concentration ratios, June – September 2003

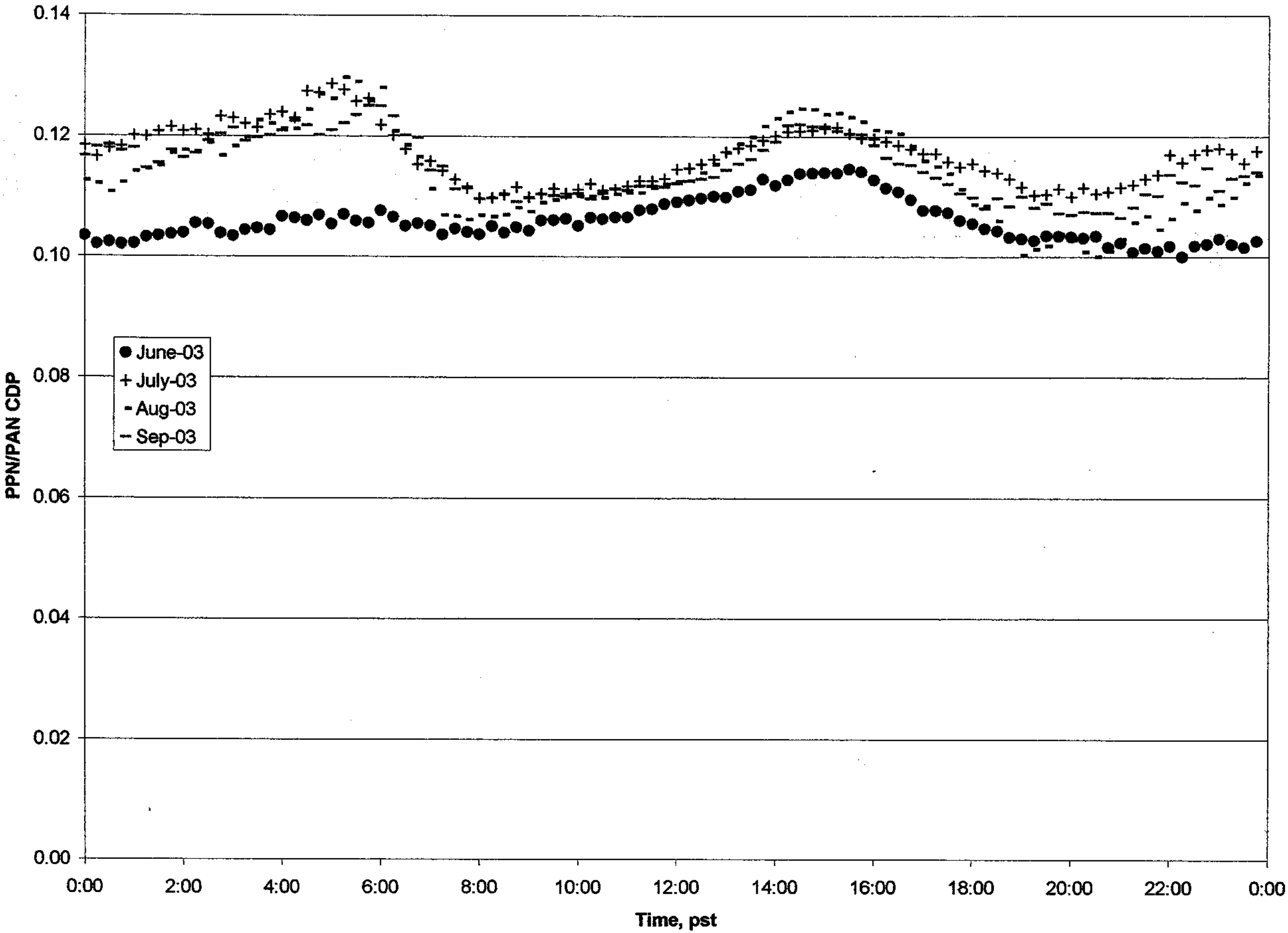

Figure 6.22 Monthly-averaged CDP of the PPN/PAN concentration ratio for June 2003, shown with standard deviations

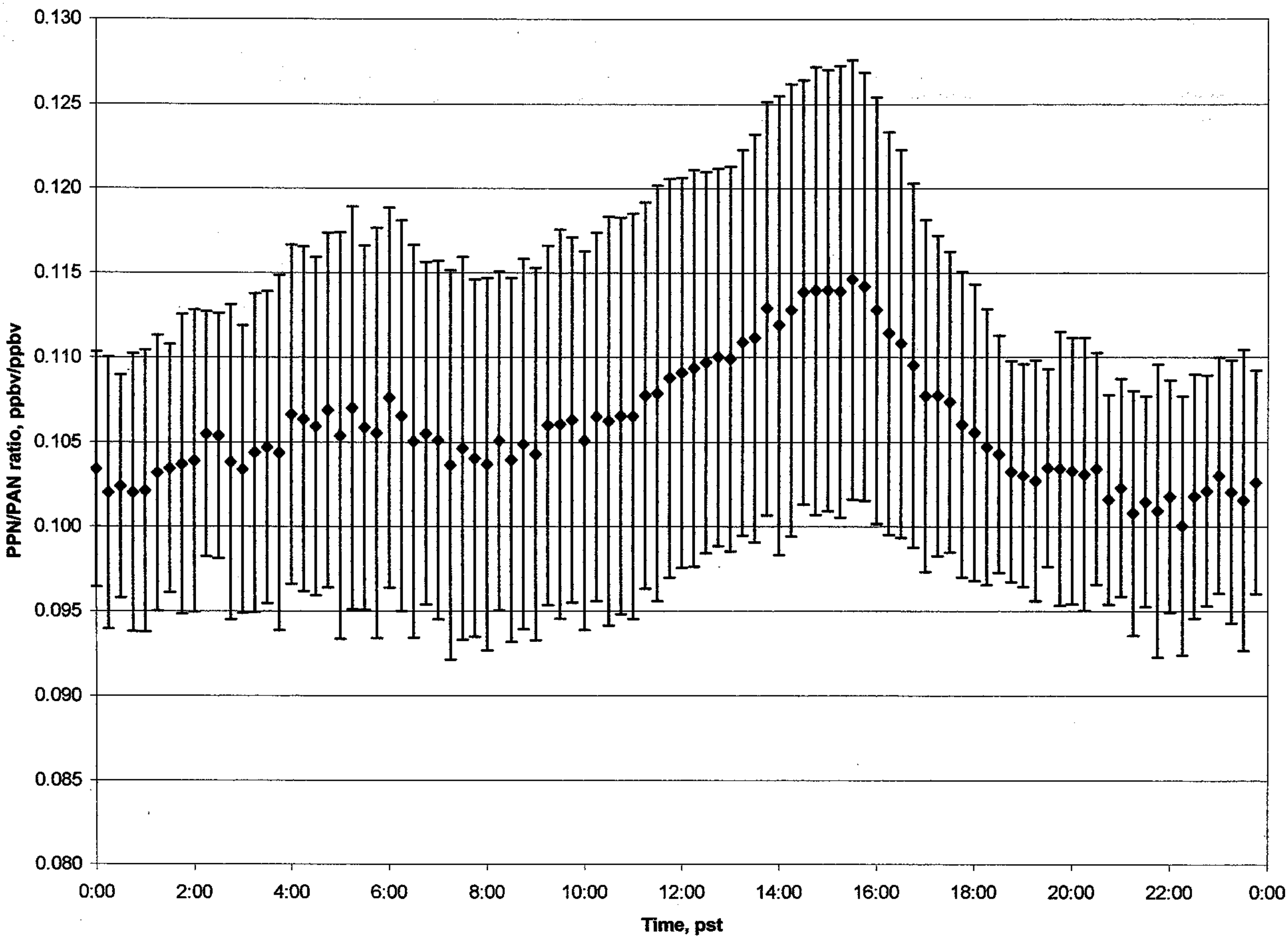

Figure 6.23 Comparison of the CDP for the PPN/PAN concentration ratios and that for PPN concentrations, 2003

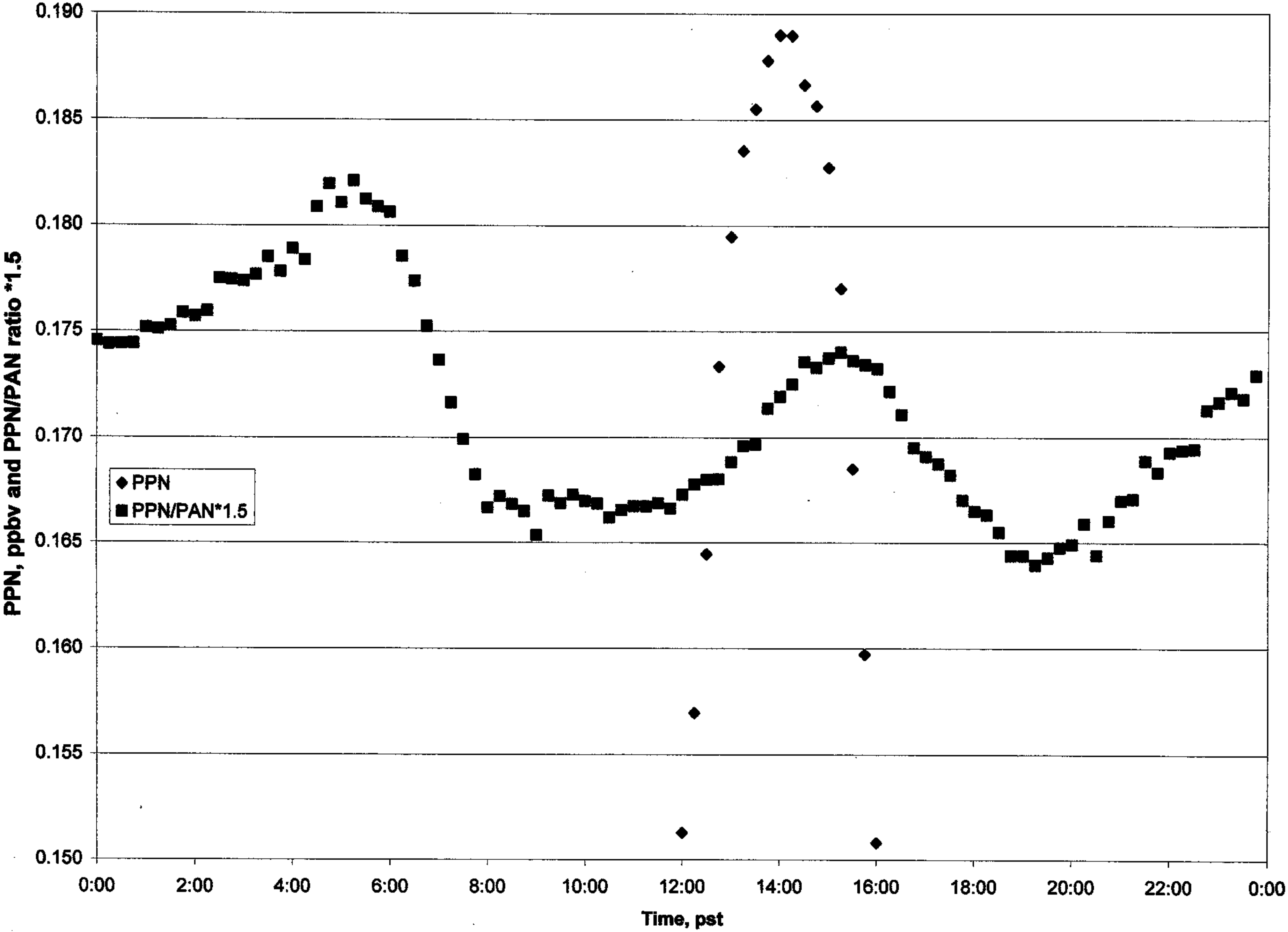

Figure 6.24 Scatterplot of PPN/PAN concentration ratios vs. PAN concentrations, 2003

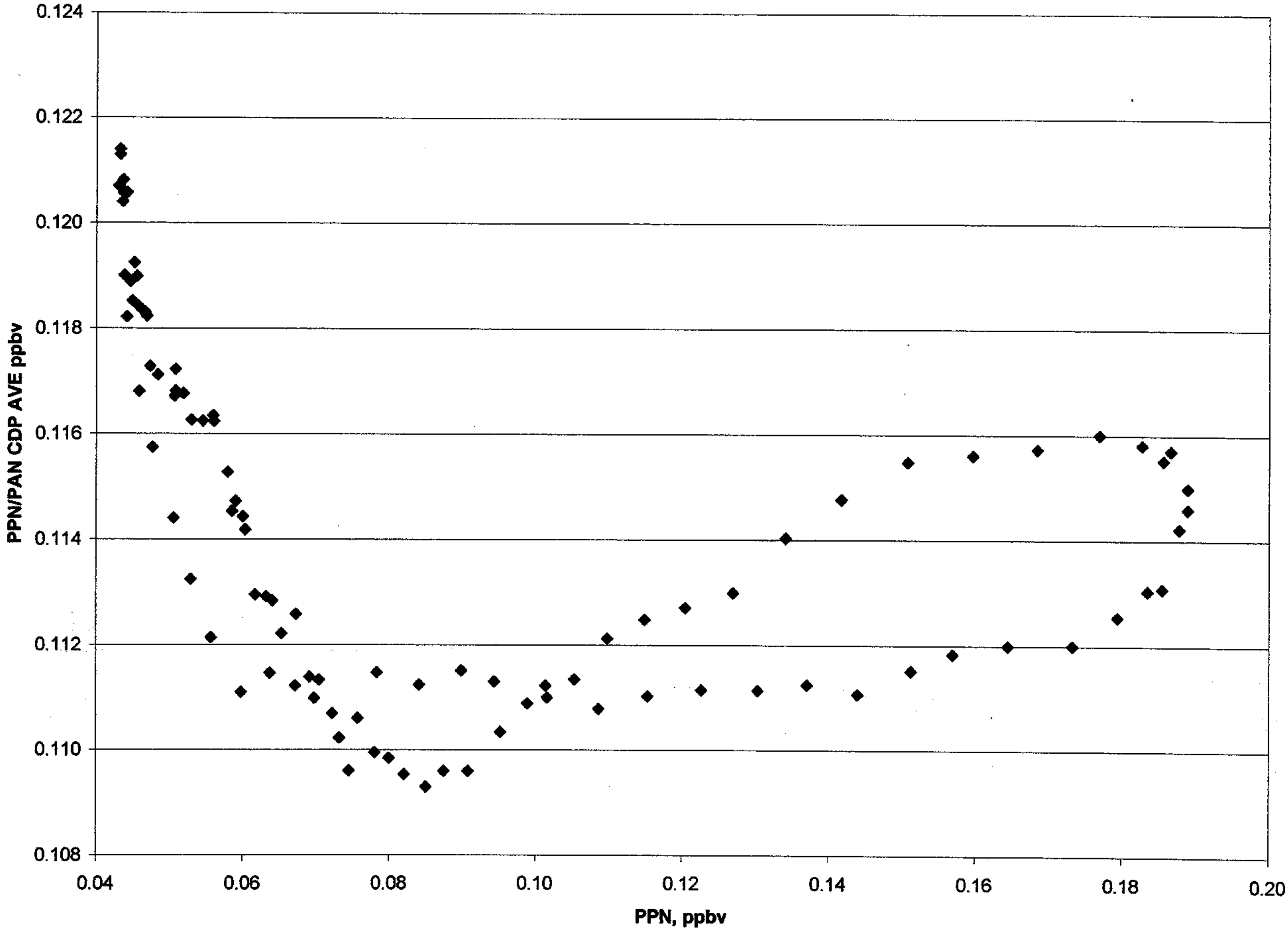

Figure 6.25 Composite diurnal profiles of the PPN/PAN ratio for each day of the week in 2002

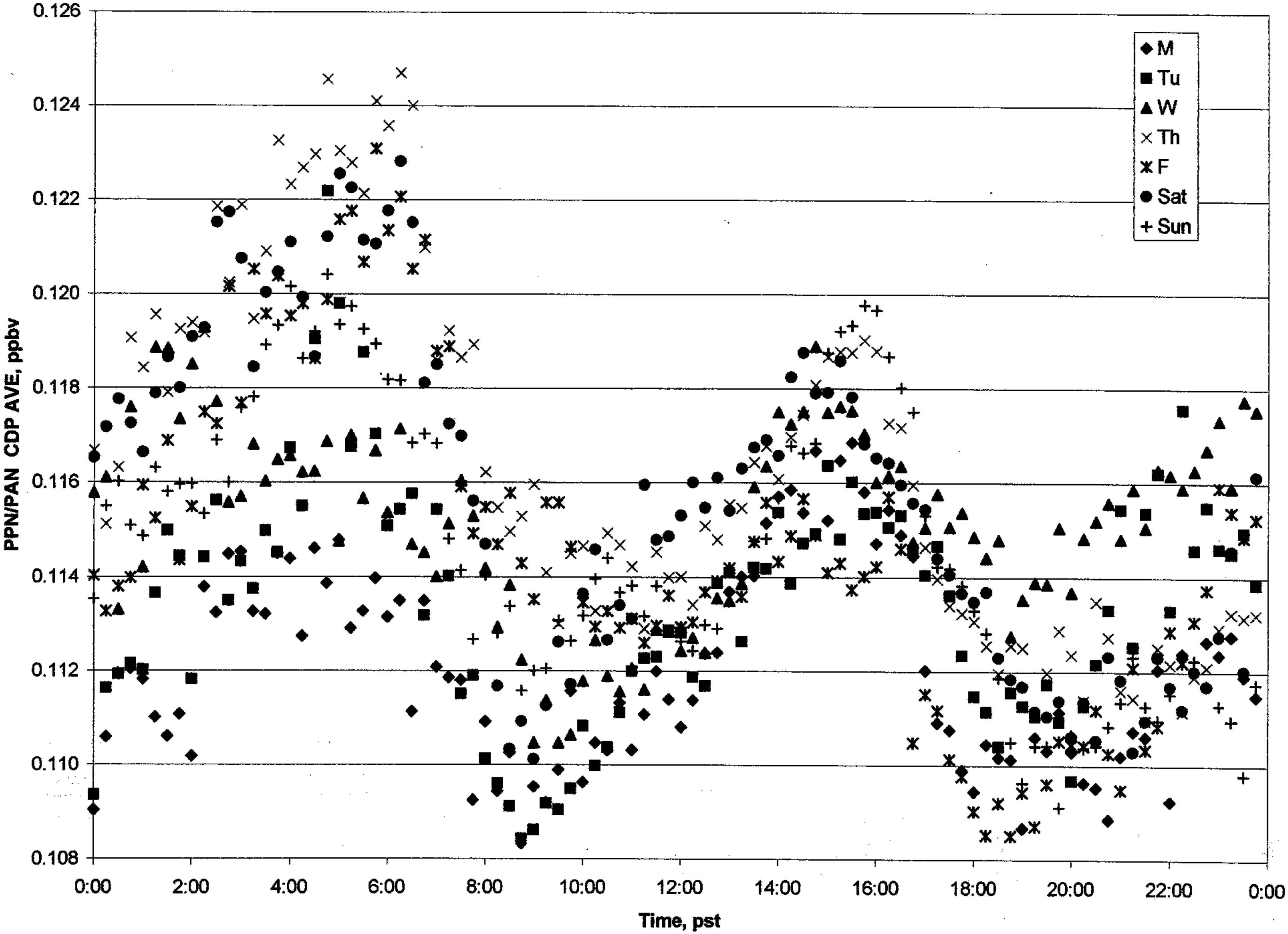

Figure 6.26 Composite diurnal profile of the PPN/PAN maxima for 2001

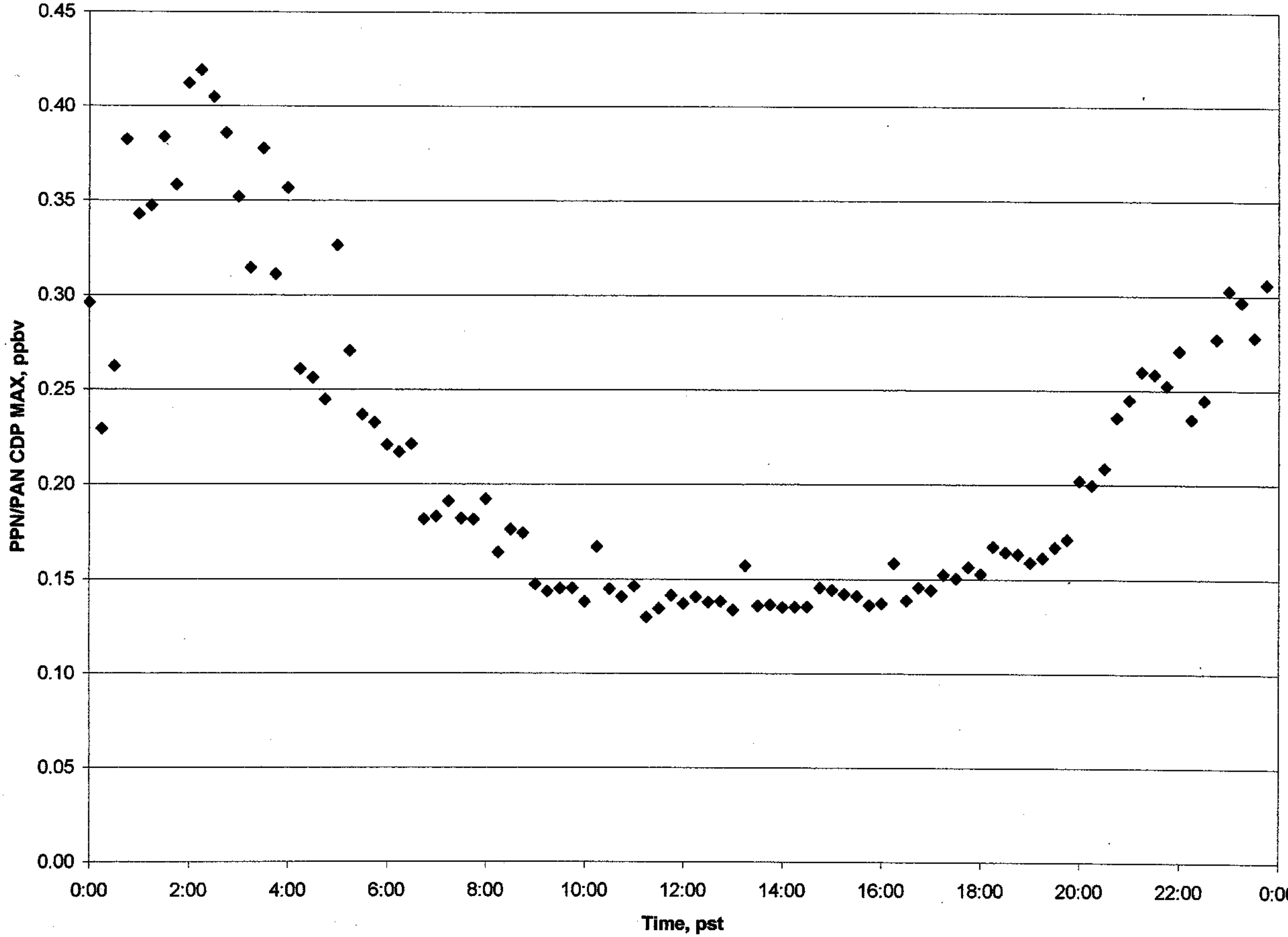

Figure 6.27 Composite diurnal profile of the PPN/PAN maxima for 2002

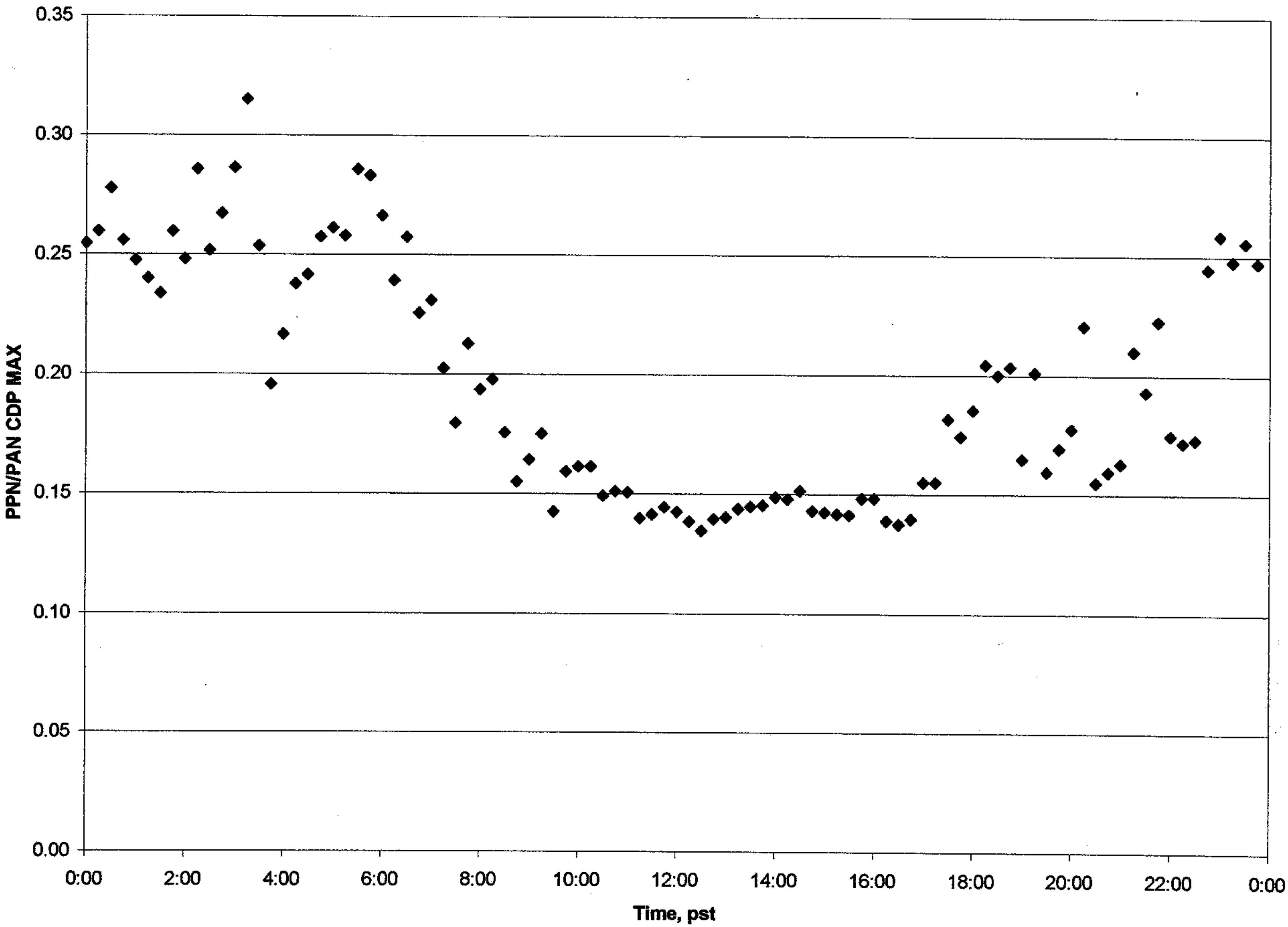

Figure 6.28 Composite diurnal profile of the PPN/PAN maxima for 2003

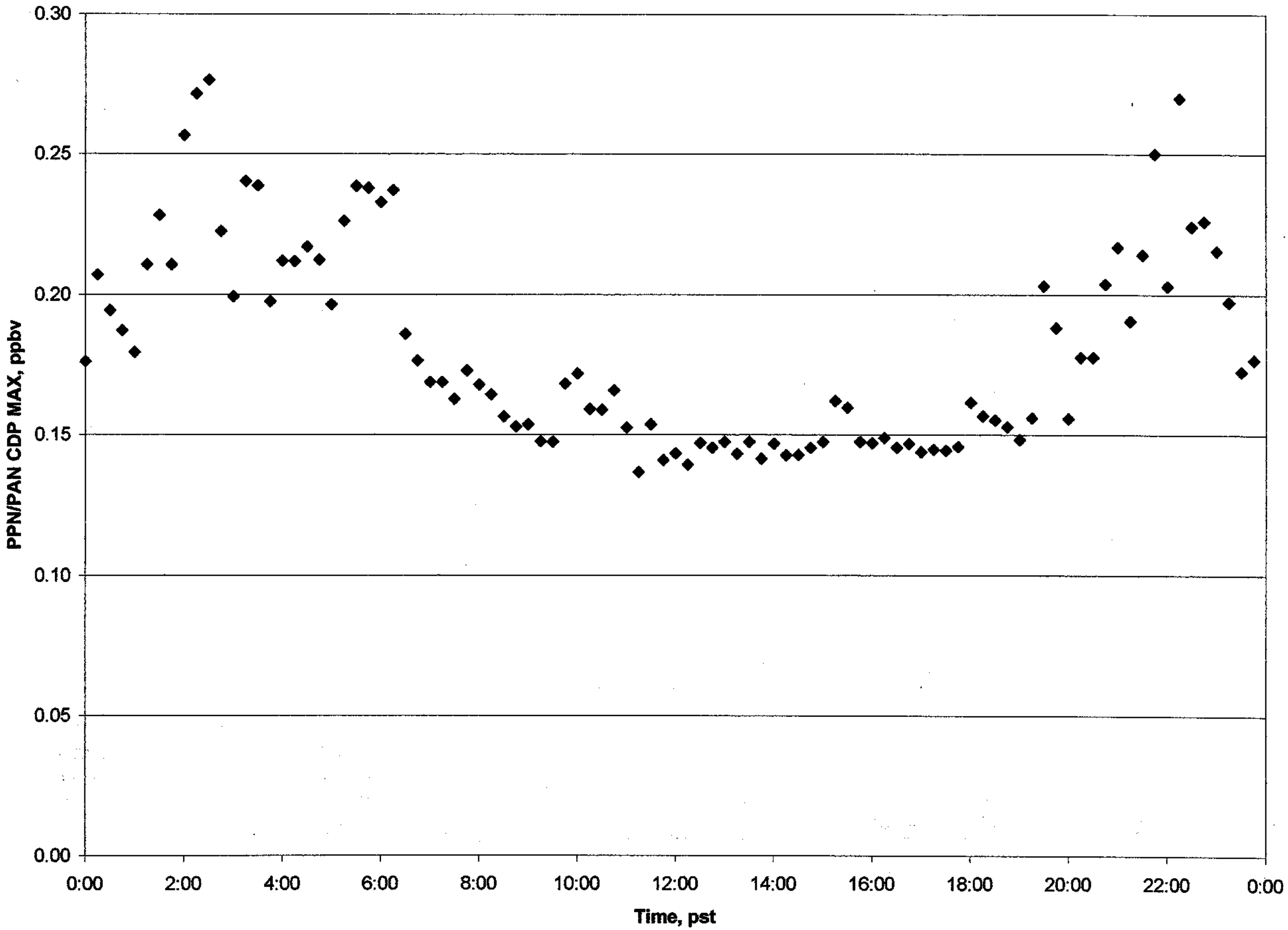

Figure 6.29 Composite diurnal profile of the PPN/PAN minima for 2001

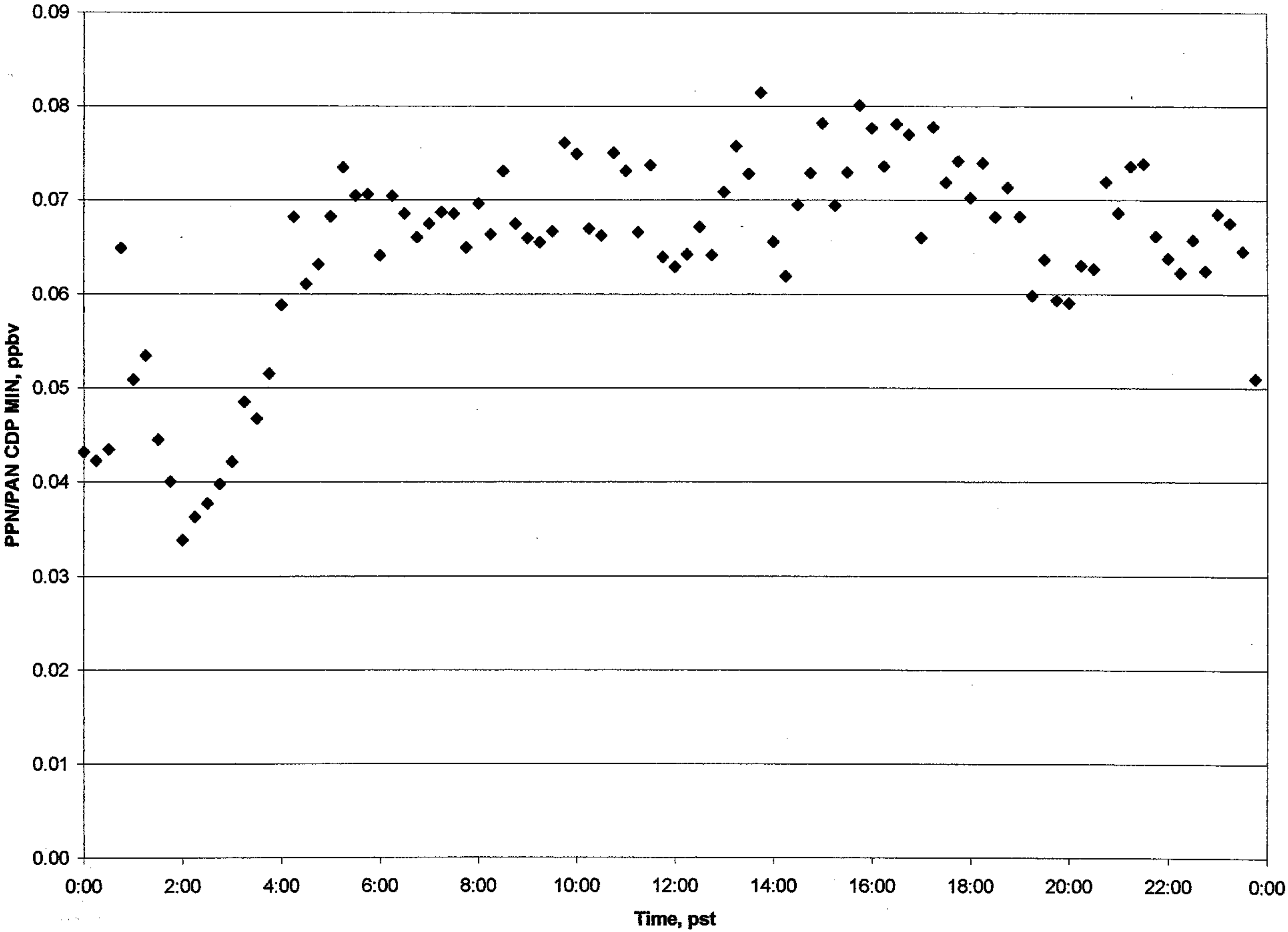

Figure 6.30 Composite diurnal profile of the PPN/PAN minima for 2002

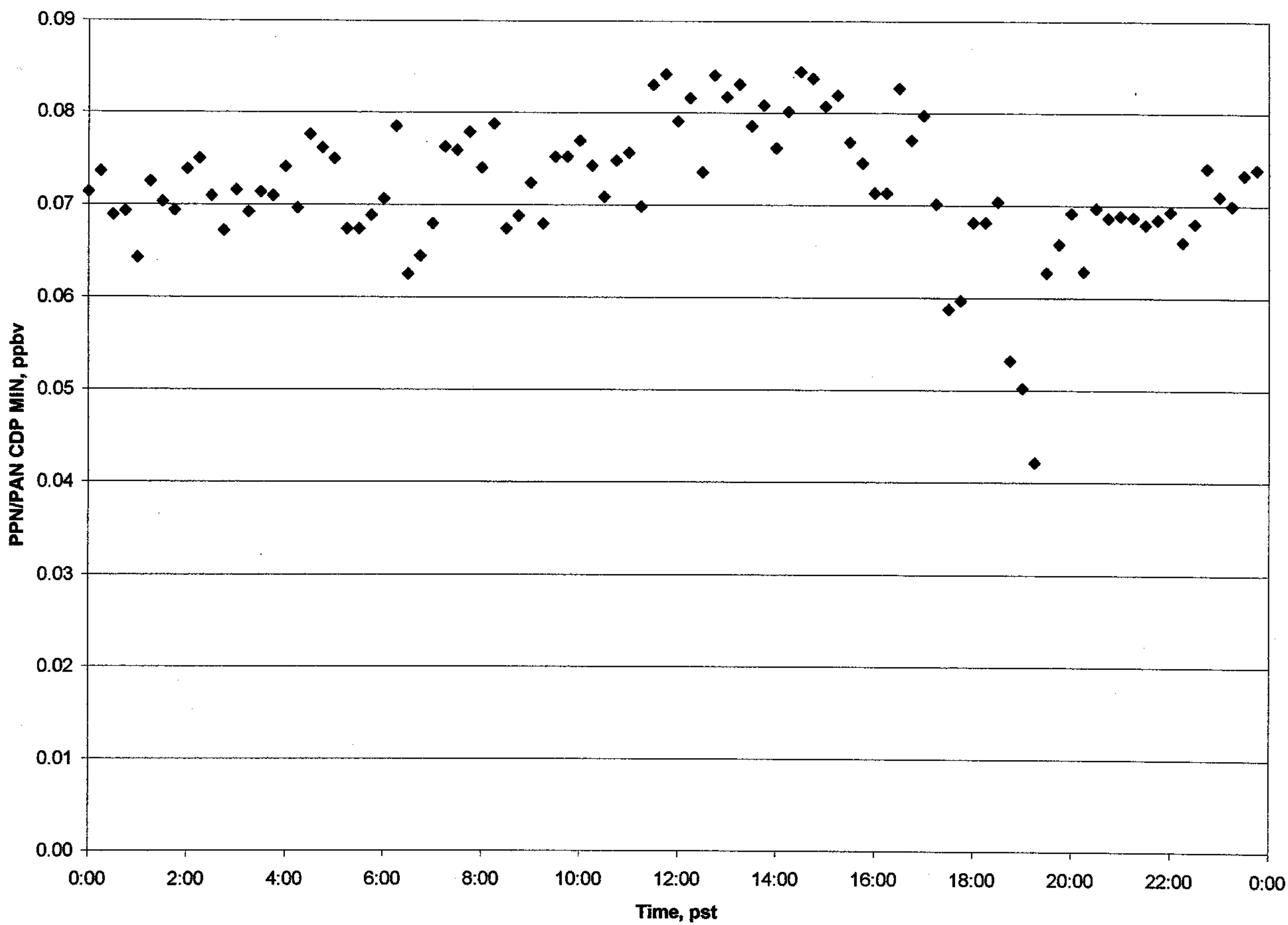

Figure 6.31 Composite diurnal profile of the PPN/PAN minima for 2003

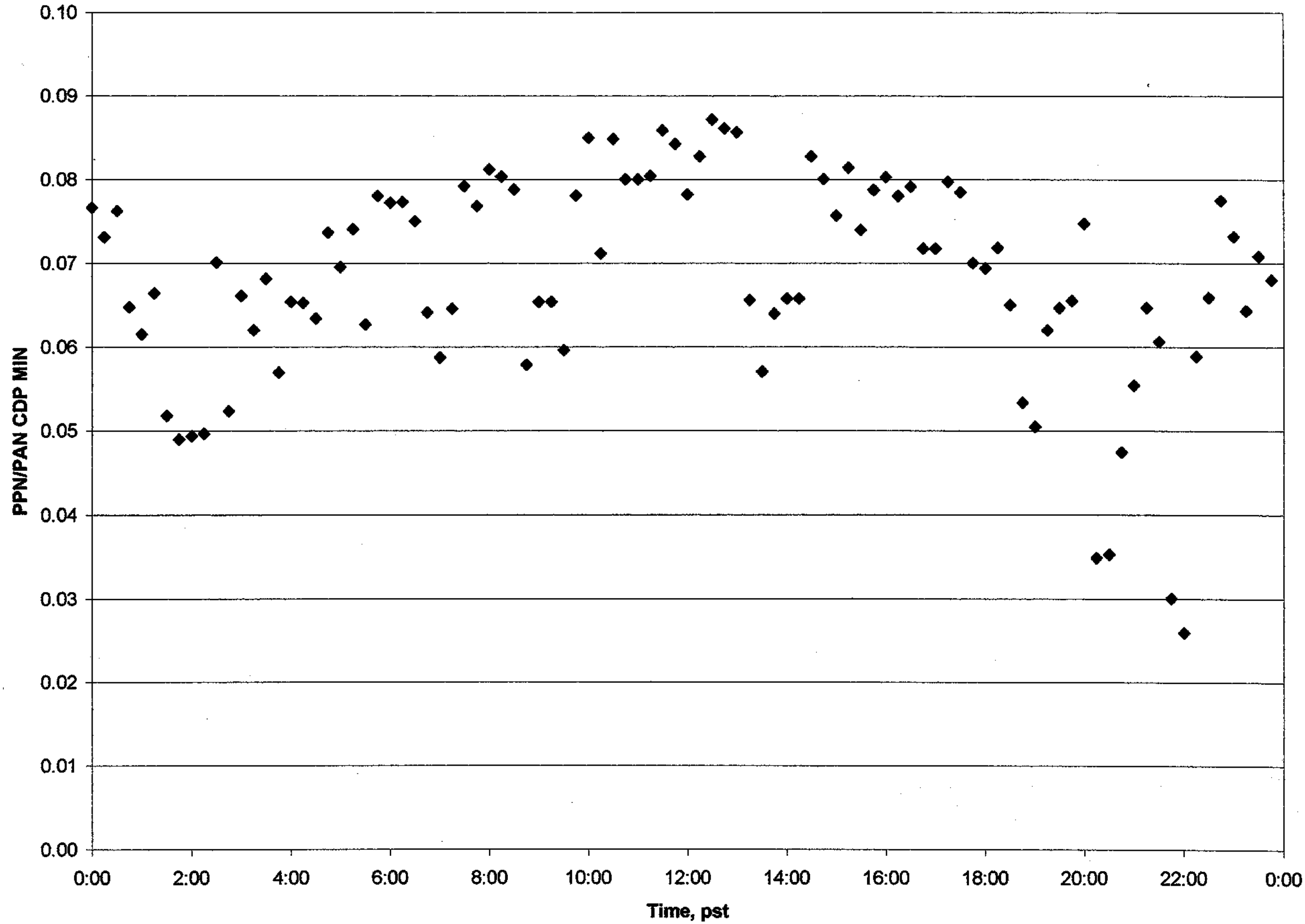

Figure 6.32 Concentrations of PAN and PPN and PPN/PAN concentration ratio, December 28 – 29, 2001

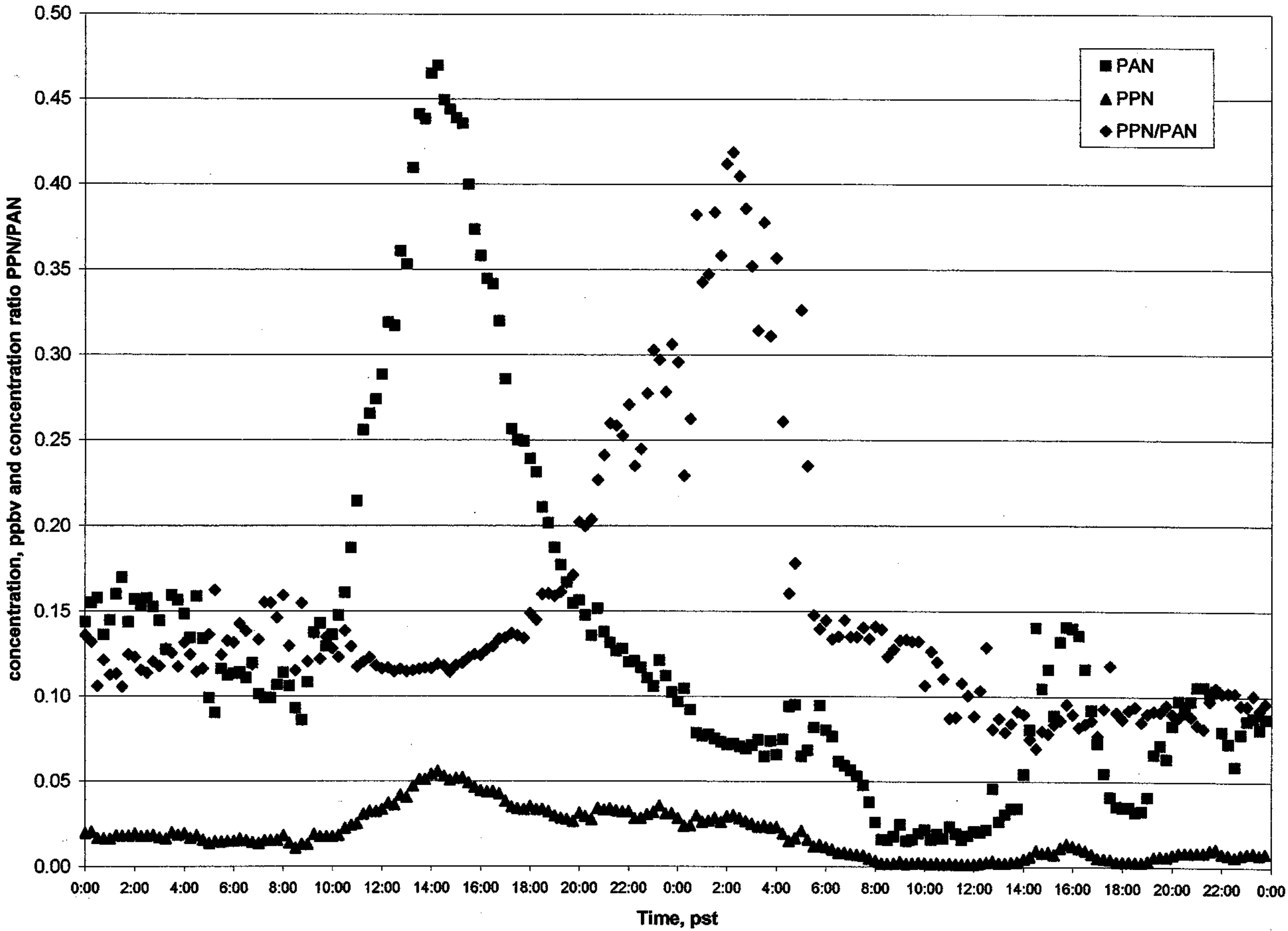

Figure 6.33 Concentrations of PAN and PPN and PPN/PAN concentration ratio, August 28 – 31, 2001